ONO Dianionic Pincer-type Ligand Precursors for the Synthesis of σ,π-Cyclooctenyl Iridium(III) Complexes: Formation Mechanism and Coordination Chemistry

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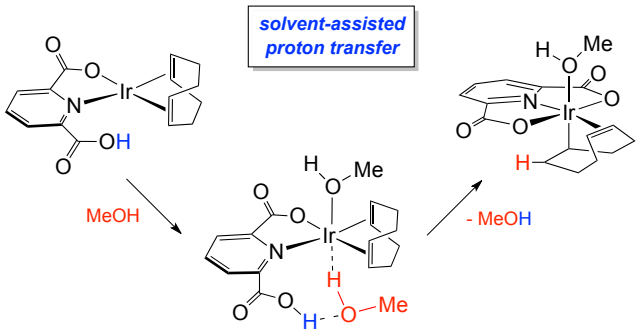
The σ,π-cyclooctenyl iridium (III) pincer compounds [Ir(κ^3-pydc-X)(1-κ-4,5-η-C_8H_{13})] (X = H (**1**), Cl, Br) have been prepared from [Ir(μ-OMe)(cod)]$_2$ and the corresponding 4-substituted pyridine-2,6-dicarboxylic acids (H_2pydc-X) or, alternatively, from their lithium salts (X = H) and [Ir(cod)(CH_3CN)$_2$]PF_6. Deuterium labeling studies in combination with theoretical calculations have shown that formation of **1** involves a metal-mediated proton transfer in the reactive intermediate [Ir(κ^2-Hpydc)(cod)], through the solvent stabilized hydrido complex [IrH(κ^3-pydc)(cod)(CH_3OH)], followed by olefin insertion. The formation of this hydrido intermediate results from the solvent-assisted proton transfer through a hydrogen-bonding network forming an eight-membered metallacycle. In contrast, reaction of [Ir(μ-OMe)(cod)]$_2$ with iminodiacetic acid derivatives, RN(CH_2COOH)$_2$, gave the stable iridium(I) mononuclear [Ir{κ^2-MeN(CH_2COOH)(CH_2COO)}(cod)] (R = Me) complex having a free carboxymethyl group, and the tetranuclear complex [Ir_4{κ^4-PhN(CH_2COO)$_2$}$_2$(cod)$_4$] (R = Ph) with doubly deprotonated ligands. The molecular structure of the related cyclooctene complex [Ir_4{κ^4-PhN(CH_2COO)$_2$}$_2$(coe)$_8$] has been determined by X-ray analysis. Reaction of **1** with monodentate N- and P-donor ligands gave the compounds [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(L)] (L = py, $BnNH_2$, PPh_3 and PMe_3). Reaction of **1** with the short-bite bis(diphenylphosphino)methane (dppm) afforded the mononuclear **1-dppm**, with an uncoordinated P-donor atom, or the dinuclear **1_2-dppm** complex as a function of the molar ratio used. Similarly, the dinuclear complexes **1_2-dppe** and **1_2-dppp** have been prepared using 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) as bridging ligands. The diphosphine-bridged dinuclear assemblies have been obtained as two diastereoisomers in a 1:1 ratio due to the chirality of the mononuclear building block. The single crystal X-ray structures of **1-py** and **1-dppm** are reported.



Keywords: pincer ligands / carboxylate ligands / reaction mechanisms / iridium

Introduction

The chemistry of pincer ligands, bearing three coordination sites providing a rigid meridional environment to the metal center, is one of the most dynamic areas in modern inorganic chemistry due to the impressive number of applications in material science and catalysis.[1] In spite of the apparent simplicity of the ligand framework, pincer ligands are valuable tools for generating metal complexes with an adequate balance of thermal stability and reactivity. Although a large number of ligands bearing C, N, P or S donor-based functionalities have been synthesized,[2] pincer ligands having O-donor fragments have been much less studied.[3] In this context, the ability of OCO and ONO trianionic pincer ligands for supporting high-oxidation-state metal complexes with vacant coordination sites, which have been recently exploited for a range of catalytic transformations, is remarkable.[4,5]

Low-valent iridium complexes have been reported to show good activity for C-H activation and functionalization processes.[6] Periana et al. have shown that octahedral Ir(III) complexes [Ir(k2-acac)2(R)(py)] (R = CH3, Ph) bearing two acetylacetonate ligands (acac), one leaving alkyl group and one accessible coordination site, efficiently catalyzed the hydroarylation of olefins, which likely proceeded via Ir(III)/Ir(V) inter-conversion.[7] O-donor ligands in these systems play an important role facilitating the access to high oxidation states by modulating the electron density at the metal centers via a hard/hard interaction or π-donating effects.[8]

Recently, iridium complexes bearing O-based dianionic pincer ligands have attracted considerable attention with regard to C-H bond activation. The robustness and stability of the ligand framework, with strongly electron donating hard oxygen atoms, can provide more facile access to the relatively high oxidation state of the metal center thereby promoting the C-H bond oxidative addition under mild conditions. Bercaw and Labinger *et al*. reported the synthesis of Ir(I) and Ir(III) complexes bearing a diphenolate-imidazolyl-carbene tridentate ligand (Chart 1, i) but no C-H bond activation chemistry was demonstrated.[9] Recently, the

same group has described the synthesis of bis(phenolate)pyridine iridium(III) pincer complexes (Chart 1, ii) and their ability to smoothly activate both intra- and intermolecular C-H bonds.[10] On the other hand, at the same time we reported the synthesis of unsaturated iridium(III) pyridinedicarboxylate pincer complexes (Chart 1, iii) which exhibited a notable catalytic activity in borylation of arenes involving C-H bond activation under thermal conditions.[11] It is noteworthy that the synthesis of some iridium and rhodium complexes containing pyridine-2,6-dicarboxylate ligands has been described but no catalytic applications were reported.[12]

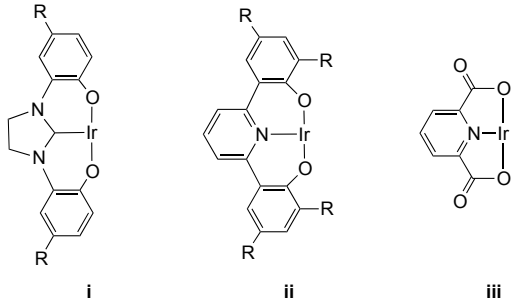


Chart 1. Ligand framework of O-based dianionic pincer iridium complexes (R = ^{t}Bu).

In the present contribution we report on the synthesis and reactivity of unsaturated σ,π-cyclooctenyl complexes [Ir(κ^3-pydc-X)(1-κ-4,5-η-C_8H_{13})] (X = H, Cl, Br). The straightforward synthesis of these unusual iridium(III) pincer complexes from pyridine-2,6-dicarboxylic acids and standard dinuclear iridium(I) starting materials, the simple ligand architecture of these complexes and their potential catalytic applications based on C-H activation, have prompted us to investigate their formation mechanism. In addition, the scope of the synthetic methodology for the preparation of iridium(III) pincer complexes derived from related dicarboxylic compounds as precursors has also been investigated.

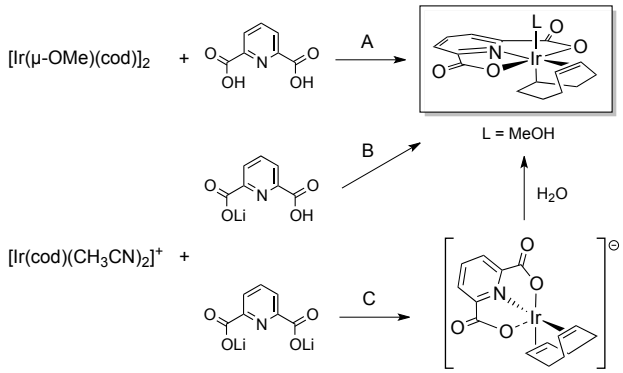
Results and Disscusion

Synthesis of pyridinedicarboxylate pincer complexes [Ir(κ^3-pydc-X)(1-κ-4,5-η-C$_8$H$_{13}$)]. The σ,π-cyclooctenyl iridium (III) compound [Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)] (**1**) can be straightforwardly prepared by reaction of 2,6-pyridinedicarboxylic acid (H_2pydc) with 0.5 molar equiv. of the dinuclear 1,5-cyclooctadiene iridium methoxy-bridged complex [Ir(μ-OMe)(cod)]$_2$ in CH_2Cl_2/MeOH at room temperature (Method A, Scheme 1). The compound was obtained as the methanol solvate **1**-MeOH, as it was confirmed by a X-ray analysis, and isolated as an air and moisture stable yellow solid in 90% yield after chromatographic purification.[11] This synthetic method is applicable for the preparation of related 4-substituted pyridine-2,6-dicarboxylate pincer complexes. Thus, reaction of complex [Ir(μ-OMe)(cod)]$_2$ with 4-chloro- or 4-bromo-pyridine-2,6-dicarboxylic acids afforded the corresponding complexes [Ir(κ^3-pydc-Cl)(1-κ-4,5-η-C$_8$H$_{13}$)] (**2**) and [Ir(κ^3-pydc-Br)(1-κ-4,5-η-C$_8$H$_{13}$)] (**3**) which were isolated as red solids in excellent yield. These complexes are scarcely soluble in most organic solvents including dichloromethane or methanol although, surprisingly, the compounds have an acceptable solubility in a 5:1 mixture of both solvents.

The σ,π-cyclooctenyl ligand in complexes **1**-**3** has been unequivocally identified by NMR spectroscopy.[13] For example, the olefinic protons and carbons (=CH) were observed as two characteristics low-field multiplet resonances at 5.87 and 5.64 ppm in the ^{1}H NMR spectrum of **3**, which correlates with those at 89.0 and 85.0 ppm in the ^{13}C{^{1}H} NMR spectrum. The Ir-*C*H resonance was easily identified in the ^{13}C APT spectrum at 14.6 ppm. Full assignment of the resonances and connectivity in the σ,π-cyclooctenyl ligand was achieved with the help of 2D ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HMBC experiments.

The stability of **1** allows for alternative synthetic approaches from cationic mononuclear iridium complexes and 2,6-pyridinedicarboxylic acid lithium salts. Thus, treatment of [Ir(cod)(CH$_3$CN)$_2$]PF$_6$ with lithium 6-carboxypicolinate (HLipydc) in CH_2Cl_2/MeOH gave **1**

in 96% without the need of chromatographic purification after removing the $LiPF_6$ salt (Method B, Scheme 1). It is noteworthy that reaction of $[Ir(cod)(CH_3CN)_2]PF_6$ with lithium pyridine-2,6-dicarboxylate (Li_2pydc) also gave **1** in excellent yield instead of the expected iridium(I) anionic complex $Li[Ir(\kappa^3\text{-pydc})(cod)]$ (Method C, Scheme 1). In this case, the formation of **1** can be explained by the presence of adventitious water in the organic solvents, which play an important role in providing the required proton for the formation of the cyclooctenyl ligand. In sharp contrast, only a very small amount of **1** was formed starting from the chloro-bridged dimer $[Ir(\mu\text{-Cl})(cod)]_2$ and pyridine-2,6-dicarboxylate lithium salts, even under heating conditions, which is consistent with the poor leaving ability of the chlorido ligand.



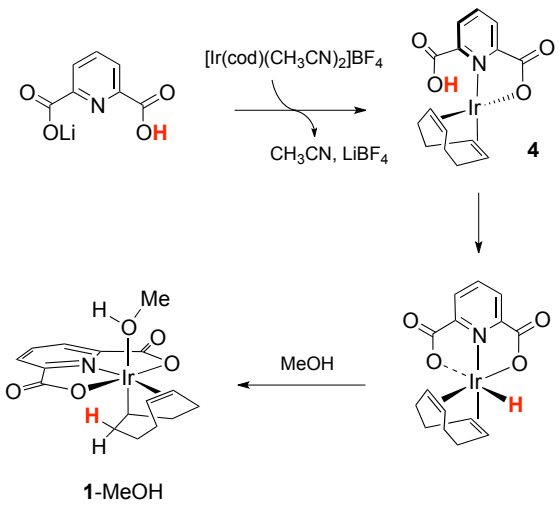
Scheme 1. Synthetic routes to $[Ir(\kappa^3\text{-pydc})(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})]$ (**1**) from 2,6-pyridinedicarboxylic acid and its lithium salts. Reactions conducted in CH_2Cl_2/MeOH (3/1).

Mechanistic studies on the formation of $[Ir(\kappa^3\text{-pydc})(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})]$. The synthesis of $[Ir(\kappa^3\text{-pydc})(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})]$ (**1**) has been investigated by NMR. Firstly, it is reasonable to propose that the protonation of the methoxido bridges in $[Ir(\mu\text{-OMe})(cod)]_2$ by H_2pydc results in the formation of the mononuclear neutral iridium(I) intermediate $[Ir(\kappa^2\text{-Hpydc})(cod)]$ (**4**) having the monodeprotonated ligand κ^2-*N,O* coordinated and an uncoordinated carboxyl group (Method A). This species should be also straightforwardly

generated by replacement of the labile acetonitrile ligands in $[Ir(cod)(CH_3CN)_2]^+$ by lithium 6-carboxypicolinate (Method B). In fact, the clean synthesis of **1** using this method further supports this proposal. The intermediate compound **4**, which is immediately formed after mixing the reagents by both methods, has been characterized in solution. The ^{1}H NMR spectrum of [Ir(κ^2-Hpydc)(cod)] (**4**) at 208 K (CD_2Cl_2/CD_3OD) features a set of four resonances at 4.26, 3.77 (=CH protons), 2.09 and 1.28 ppm (>CH_2, *exo* and *endo* protons), which is in full agreement with the integrity of the cyclooctadiene ligand. Furthermore, the HR ESI-MS showed the peaks at m/z 490.0633 (ESI+) and 466.0672 (ESI-) corresponding to ions $[M + Na]^+$ and $[M - H]^-$, respectively. Warming up to room temperature resulted in broad resonances although no evidence of proton transfer from the carboxyl group to the cod ligand was immediately observed. Interestingly, the formation of the related [Ir(κ^2-Hpydc-Br)(cod)] species was also observed under similar conditions.

A plausible mechanism for the proton transfer leading to the cyclooctenyl ligand is a metal-mediated process. Thus, the protonation of the iridium center in [Ir(κ^2-Hpydc)(cod)] (**4**) by the free -COOH arm of the tridentate ligand, formally an oxidative addition, should result in an octahedral iridium(III) hydrido complex [IrH(κ^3-pydc)(cod)]. Subsequent insertion of one of the C=C bonds into the Ir-H bond would account for the formation of **1** (Scheme 2). In this context, it is worth mentioning that the oxidative addition of carboxylic acids to iridium(I) complexes is a well documented process.[14]

The synthesis of **1** from Li_2pydc, where traces of adventitious water could act as proton source (Method C), requires further comments. Although reaction of Li_2pydc with H_2O to give back LiHpydc is possible, most probably, the protonation of the carboxylate free arm in the anionic complex Li[Ir(κ^2-pydc)(cod)] by H_2O to give [Ir(κ^2-Hpydc)(cod)] (**4**) and LiOH is taking place. The direct protonation of the iridium center by H_2O in the strong nucleophilic anionic complex to give a hydrido intermediate is a less likely pathway.[15]



Scheme 2. Proposed mechanism for the formation of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(CH_3OH)] (**1**-MeOH).

In order to shed light on the operating mechanism for the proton transfer we have prepared the deuterium labeled compound [Ir(κ^3-pydc)(1-κ-4,5-η-$C_8H_{12}D$)] (**1-*d*^{1}**) by two different methods. Thus, reaction of [Ir(cod)(CH_3CN)$_2$]PF_6 with lithium pyridine-2,6-dicarboxylate (Li_2pydc) in the presence of D_2O resulted in the complete incorporation of deuterium into the cyclooctenyl ligand (Method C). Interestingly, **1-*d*^{1}** can be also prepared from [Ir(μ-OMe)(cod)]$_2$ and H_2pydc in CD_2Cl_2/CD_3OD (Method A). The presence of the $C_8H_{12}D$ cyclooctenyl ligand in **1-*d*^{1}** was confirmed both in the $^{13}C\{^1H\}$ NMR, that showed the expected deuterium coupled triplet resonance at 34.73 ppm ($J_{C\text{-}D}$ = 19.0 Hz), and in the ^2H NMR at 1.21 ppm. The *endo* and *exo* protons (8-H) of the resulting >CH_2 next to the Ir-C bond in **1** have been identified at 0.92 (tt, $J_{H\text{-}H}$ = 13.9 and 2.2 Hz) and -0.01 ppm (ddd, $J_{H\text{-}H}$ = 13.9, 7.3 and 3.6 Hz), respectively (Figure 1a).[11] The triplet feature of the 8-H-*endo* resonance is due to two alike large couplings with 8-H-*exo* and one of the adjacent H-7 protons with an axial-axial relationship. This assignment is also consistent with the observation that in cyclooctenyl ligands with a metallo-chair conformation the low-shift proton of a geminal pair is located at the face of the cyclooctenyl ligand opposite to the metal

fragment.[16] Thus, the lack of the resonance at δ 0.92 ppm in the ^{1}H NMR spectrum of **1-*d*^{1}** (Figure 1b), assigned to the 8-H-*endo* proton, supports the proposed hydride/insertion mechanism as the migratory insertion proceeds with *cis* stereochemistry.

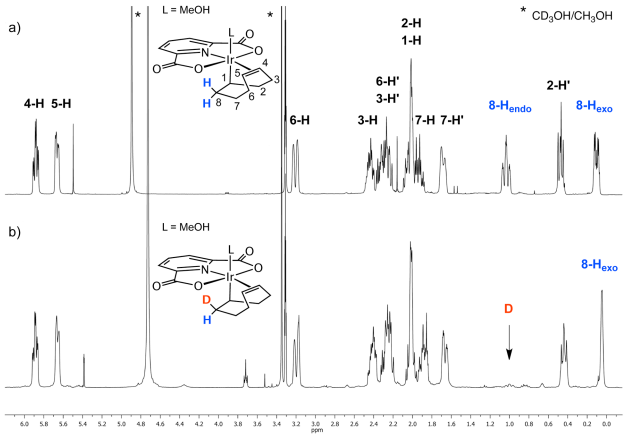


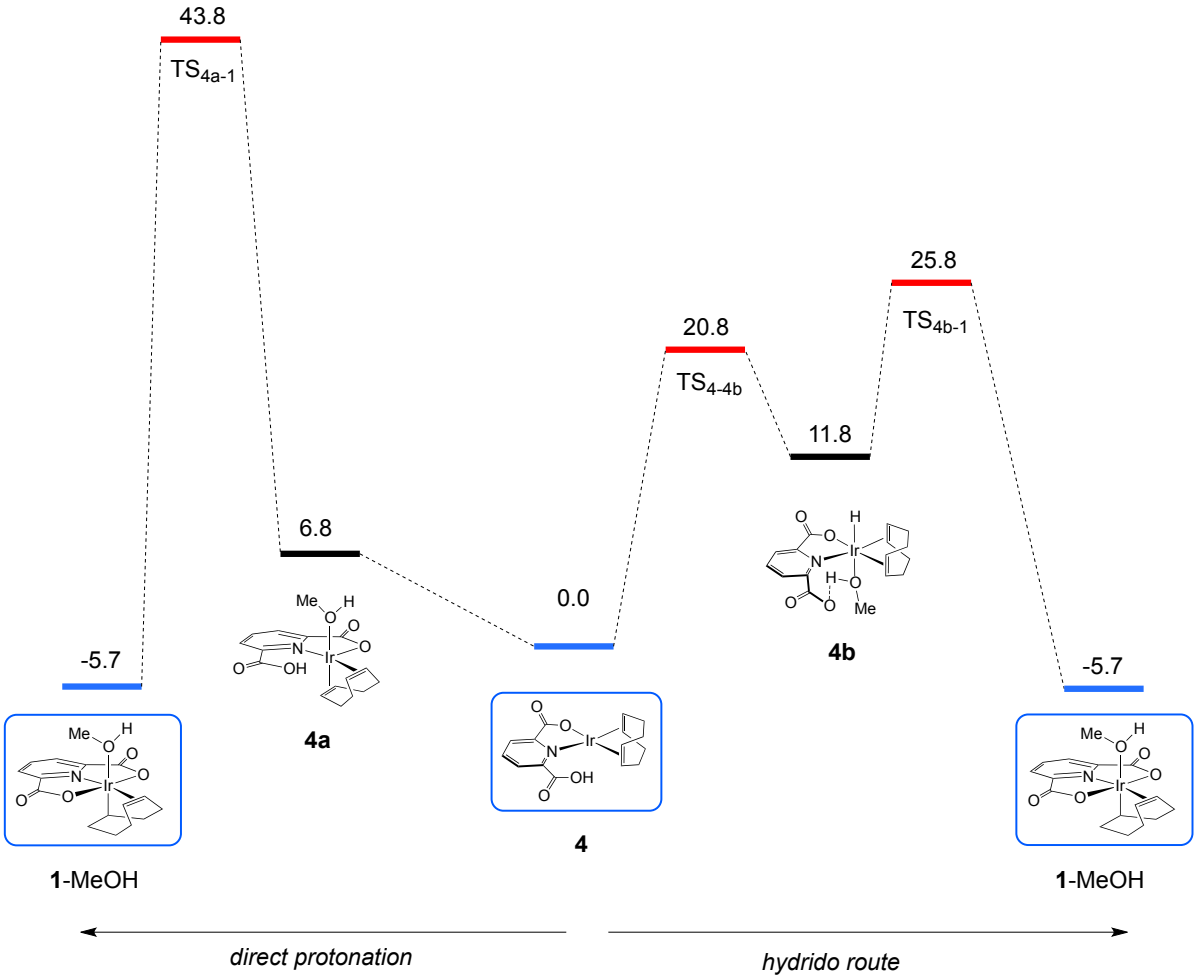
Figure 1. Cyclooctenyl region of the ^{1}H NMR spectra of: a) [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**) and, b) [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{12}D)] (**1-*d*^{1}**).

Unfortunately, we have not been able to observe any hydrido intermediate by monitoring the reactions leading to complexes **1**-**3**. In addition, the stereochemistry of **1-*d*^{1}** is also compatible with the intramolecular direct protonation of the cycloctadiene ligand by the carboxyl group. In fact, the direct protonation of cycloctadiene on electron-rich nickel(0) complexes has been demonstrated.[16] On the other hand, the *exo* nucleophilic attack by methoxide on cyclooctadiene palladium complexes to give chlorido-bridged cyclooctenylmethoxy palladium dimers has been also described.[17]

DFT calculations on the proton transfer mechanism in [Ir(κ^2-Hpydc)(cod)]. In order to ascertain the proton transfer mechanism in [Ir(κ^2-Hpydc)(cod)] (**4**) leading to the formation of the σ,π-cyclooctenyl iridium (III) compound [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**) as the methanol solvate, **1**-MeOH, a detailed computational study using DFT calculations has been carried out.

The optimized structure of the initial intermediate [Ir(κ^2-Hpydc)(cod)] (**4**) shows the expected square planar coordination environment for an Ir(I) center which is bonded to cod and a 6-carboxypicolinato ligand κ^2-*N,O* coordinated. The remaining uncoordinated carboxyl group is located out of the molecular plane and directed away from the iridium center. A prominent feature of the structure of the final Ir(III) reaction product **1**-MeOH is that the 2,6-pyridinedicarboxylato ligand plane runs eventually parallel to the unchanged double bond of the σ,π-cyclooctenyl ligand, in a 90 degrees turn relative to the starting position in **4**. This fact along with the coordination of a methanol molecule to the final complex, suggests some complexity in the reaction mechanism.

Assuming that the parallel reorientation of the ligand could occur before the proton transfer to the cyclooctadiene ligand, rotation of the 6-carboxypicolinato ligand in **4** and coordination of a MeOH molecule leads to **4a** which is just 6.8 kcal mol^{-1} above the starting mononuclear complex and has been shown to be a minimum in the potential energy surface of the molecule. The formation of the cyclooctenyl group could proceed by either the formation of a hydrido intermediate followed by insertion of the hydrido ligand into the double bond or by a direct protonation of the double bond by the acidic carboxyl group. Interestingly, the carboxyl group in **4a** has the required orientation for both processes. Scanning of the Ir-H distance from the carboxyl group in the search for a potential hydrido is always uphill and any full optimization reverts to **4a**. On the other hand, scanning the C(olefin)-H distance leads to a transition state $TS_{4a\text{-}1}$ at a relative energy of 37.0 kcal mol^{-1} which connects with the final complex **1**-MeOH. Although this is a possible reaction pathway, the overall activation energy of 43.8 kcal mol^{-1} from **4** makes it highly unfavorable (Scheme 3, left side).



Scheme 3. DFT calculated ΔE (in kcal mol^{-1}) energy profile for the proton transfer mechanisms in [Ir(κ^2-Hpydc)(cod)] (**4**) leading to the formation of the methanol solvate of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**).

A possible pathway can be provided by participation of hydrido iridium(III) intermediates derived from **4**. The tridentate 2,6-pyridinedicarboxylate ligand can adopt, in principle, either *fac* or a *mer* disposition in an octahedral geometry. The geometry optimization of a *fac* mononuclear hydrido isomer leads to a high energy (25.2 kcal mol^{-1} relative to **4**) and strongly distorted structure **4d**, which shows a pseudooctahedral geometry where the 2,6-pyridinedicarboxylate ligand spans roughly three *fac*-disposed coordination sites in a very strained conformation (Figure 2). This high energy suggests that **4d** is not a viable intermediate. Much more stable is the pseudooctahedral *mer* hydrido isomer **4c**, where the

three donor atoms of the 2,6-pyridinedicarboxylate ligand are coplanar to one of the double bonds of the cyclooctadiene ligand, with the hydrido ligand *trans* to the other double bond of the diolefin which is very weakly coordinated. In spite of this structure being very close in energy to the starting compound (+ 3.1 kcal mol^{-1}), it has not the required stereochemistry to produce the insertion final product. The C=C double bond lies perpendicular to the Ir-H bond and, consequently, the insertion process requires a substantial amount of activation energy, $TS_{4c\text{-}1}$ (33.5 kcal/mol), which makes it highly unfavorable again.

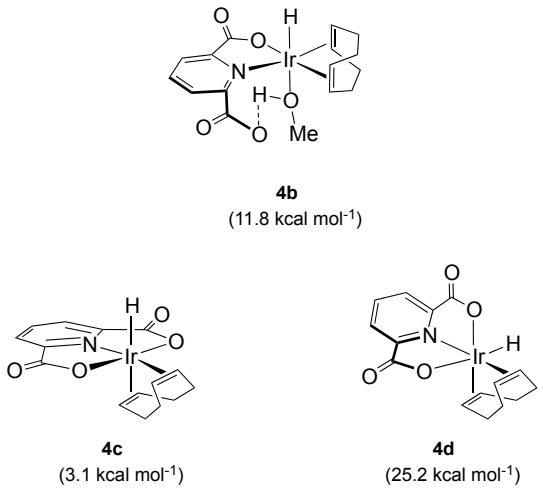


Figure 2. DFT computed energies (kcal mol^{-1}) relatives to [Ir(κ^2-Hpydc)(cod)] (**4**) for a *fac* (**4d**), *mer* (**4c**) and methanol stabilized (**4b**) isomers of the hydrido complex [IrH(κ^3-pydc)(cod)].

On the light of these results, alternative reaction pathways with explicit participation of the solvent have been explored. A more accessible pathway to the insertion process is provided via the hydrido complex **4b** stabilized by a methanol molecule (Figure 2). This intermediate has lower energy than **4d** (11.8 kcal mol^{-1} relative to **4**) and features a pseudooctahedral coordination geometry with a methanol molecule coordinated (Ir-O, 2.25 Å) *trans* to the hydrido ligand and at hydrogen bond distance of an uncoordinated carboxylate group (O···H, 1.45 Å) of the pyridine-2,6-dicarboxylate ligand κ^2-*N,O* coordinated. The coordination of

methanol and the hydrogen bond to the uncoordinated carboxylate group provides a relief to the strain observed for the tridentate pyridine-2,6-dicarboxylate ligand in **4d**. In support of the stabilizing role of the methanol, calculations of a similar structure using a molecule of thf instead of methanol ends in dissociation of the thf molecule and a hydrido complex with a similar geometry to the strained **4d**. In addition, the formation of the final insertion product bearing a thf ligand instead of methanol, **1**-thf, is just 3.4 kcal mol^{-1} exothermic in contrast to the 5.7 kcal mol^{-1} released in the formation of **1**-MeOH. This consistent with the very long reaction times required (5 days at room temperature) for the formation of **1** from $[Ir(\mu\text{-}OMe)(cod)]_2$ and H_2pydc using thf as a solvent.

A transition state $TS_{4b\text{-}1}$ located at activation energy of 14 kcal/mol from **4b** (25.8 kcal mol^{-1} global) leads to the insertion product **1**-MeOH (Scheme 3, right side). This the lowest activation barrier found. Eventually, although this hydrido complex is somewhat less stable tan **4c** it opens a kinetically more feasible pathway of reaction. In any case formation of the intermediate hydrido complexes is endoergic which agree with the fact that they remain unobserved during the reaction.

The formation of the hydrido intermediate **4b** from **4** has also been studied. Scanning both the direct and the reverse processes in the search of the corresponding transition structure ends up in the intermediate **4a**. Although the stabilizing role of methanol is required to outline a reasonable reaction pathway to **1**-MeOH, the search of a transition state from **4** to **4b** using just one methanol molecule has been fruitless. The reaction has been studied with two molecules of methanol taking part in the process, one leading to the coordinated molecule of methanol in the intermediate **4b** and another one as an intervening mediator in the proton transfer of the carboxylic proton to the iridium atom. This has allowed to find the transition structure $TS_{4\text{-}4b}$ which evidence that the process for the formation of the Ir(III) hydrido intermediate take place by simultaneous transfer of the carboxylic proton to a

methanol molecule which transfers its own proton to the iridium center in a concerted way through an eight-membered metallacycle (Figure 3). The geometry of the transition state is quite advanced towards the formation of the hydrido complex as there is only 9 kcal/mole of difference between them and its formation is endothermic relative to the starting compound **4**. The distances of the transferred proton between the carboxyl and the methanol are 1.50 Å to the carboxyl oxygen atom and 1.04 Å to the methanol oxygen atom. On the other hand the hydrido ligand is located at 1.66 Å of the iridium atom (1.56 Å in the final product) and at 1.43 Å of the methanol oxygen atom. The moderate activation energy (20.8 kcal mol^{-1}, Scheme 3, right side) for the proton transfer process along with that involved in the transition from the hydrido complex to the final species (14 kcal mol^{-1}) fully accounts for the long reaction times required to drive the reaction to completion.

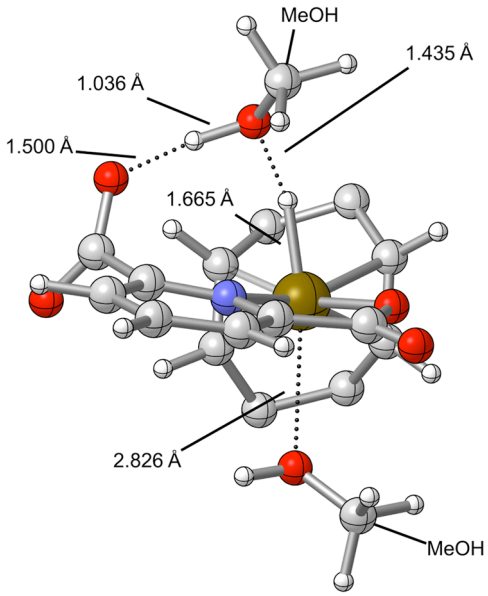


Figure 3. Structure for the transition state $TS_{4\text{-}4b}$ (some hydrogen atoms have been omitted for clarity).

Interestingly, solvent-mediated proton transfer has been recently reported to be involved in a series of processes such as formation of hydrido intermediates,[18] heterolytic hydrogen

splitting,[19] alkyne to vinylidene isomerization,[20] addition reactions[21] or H/D exchange,[22] among others.

Imino- and pyridine- diacetic derivatives as potential ONO pincer ligand precursors. In order to investigate the key factors behind the synthesis of these unusual unsaturated σ,π-cyclooctenyl iridium(III) complexes, we have studied the potential of other dicarboxylic acids for the preparation of related complexes having different pincer ligands. In particular, we have used iminodiacetic acids derivatives, $RN(CH_2COOH)_2$ (R = Me, Ph), as precursors for dianionic tridentate pincer ONO ligands. In contrast to the rigidity of 2,6-pyridinedicarboxylate, the remarkable flexibility of these ligands allows for the accommodation of different coordination environments and in fact, both *fac*[23] and *mer*[24] dispositions have been found in octahedral transition metal complexes (R = Me).

Reaction of $[Ir(\mu\text{-OMe})(cod)]_2$ with N-methyliminodiacetic acid in THF for 3 h at 50 °C gave an orange solution from which compound $[Ir\{\kappa^2\text{-}MeN(CH_2COOH)(CH_2COO)\}(cod)]$ (**5**) was isolated as an air-sensitive yellow-orange solid in good yield. Compound **5** is silent under ESI conditions and satisfactory elemental analyses could not be obtained because of its air sensitivity. However, the mononuclear formulation relays on key features of the NMR spectra. The integrity of the cod ligand in **5** became evident both in the ^1H and $^{13}C\{^1H\}$ NMR spectra (CD_3OD) that showed four well-defined resonances for the =CH protons and carbons which denotes the lack of symmetry in the molecule. Most probably **5** is a neutral iridium(I) species having a monodeprotonated N-methyliminodiacetic acid, κ^2-*N,O* coordinated, and a free carboxymethyl group (Figure 4).[25] The ^1H-^1H COSY related resonances at 5.00/4.85 and 4.63/4.32 ppm correspond to the =CH protons of the double bonds *trans* to the N and O atoms, respectively.[26] The inequivalent $>CH_2$ of the 2-((carboxymethyl)(methyl)amino)acetate ligand were observed at 71.2 and 69.0 ppm in the $^{13}C\{^1H\}$ NMR and as two AB quartets centered at 3.83 and 3.68 ppm ($J_{AB} \approx 16$ Hz) in the ^1H

NMR spectra. Interestingly, two protons of each AB system are mutually coupled (J_{H-H} = 1.8 Hz) resulting in a set of resonances with an unusual shape (Figure 4). The carboxyl group in **5** was not observed probably due to H/D exchange with CD_3OD.

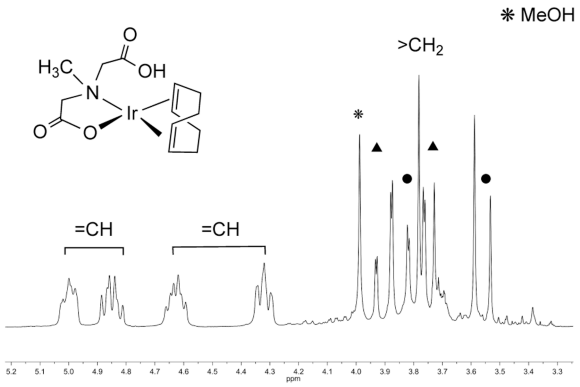


Figure 4. Selected region of the ^{1}H NMR spectrum of [Ir{κ^2-MeN(CH_2COOH)(CH_2COO)}(cod)] (**5**).

Compound **5** is formally an analogue of the intermediate species [Ir(κ^2-Hpydc)(cod)] proposed in the formation of **1**. However, the intramolecular proton transfer to the iridium center from the carboxyl group in **5** does not take place and the formation of a related σ,π-cyclooctenyl iridium(III) complex was not observed. A comparison of the acidic strength of H_2pydc (pK_{a1} = 2.10 and pK_{a2} = 4.38)[27] and MeN(CH_2COOH)$_2$ (pK_{a1} = 2.50, pK_{a2} = 9.50)[28] evidenced the less acidic character of N-methyliminodiacetic acid. Despite having a very similar first acid dissociation constant, K_{a1}, the second acid dissociation constant, K_{a2}, differs by five orders of magnitude. Thus, the acidity of the COOH proton appears to play a key role in the proton transfer process which is in full agreement with the behavior observed in oxidation additions reactions of carboxylic acids to [Ir(cod)(PMe_3)$_3$]Cl.[14b] Interestingly, the related N-phenyliminodiacetic acid, PhN(CH_2COOH)$_2$, has very similar acidic properties to H_2pydc (pK_{a1} = 2.40, pK_{a2} = 4.96)[29] and then, its reactivity has been investigated.

Addition of a methanol solution of PhN(CH_2COOH)$_2$ to a solution of [Ir(μ-OMe)(cod)]$_2$ in dichloromethane resulted in the formation of a red solid, compound **6**, irrespective of the

stoichiometry ratio (1:1 or 2:1). The infrared spectrum of **6** did not show any broad absorption in the -OH stretching region, which confirms that both carboxyl groups have been deprotonated. Unfortunately, the low solubility of this compound precludes further characterization by NMR. In the same way, reaction of the related cyclooctene iridium hydroxy-bridged complex $[Ir(\mu\text{-}OH)(coe)_2]_2$ with $PhN(CH_2COOH)_2$ under the same conditions gave an insoluble yellow-orange solid that has been characterized as the tetranuclear complex $[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(coe)_8]$ (**7**) by a single-crystal X-ray diffraction study. The formation of **7** probably results from the fast intermolecular deprotonation of the free -COOH arm by $[Ir(\mu\text{-}OH)(coe)_2]_2$ in the likely intermediate $[Ir\{\kappa^2\text{-}PhN(CH_2COOH)(CH_2COO)\}(coe)_2]$. The IR spectra of compounds **6** and **7** are comparable which allow us to propose a similar tetranuclear formulation for $[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(cod)_4]$ (**6**) with a closely related structure derived from the replacement of coe ligands by cod. Both complexes were obtained in 80% and 90% yields, respectively, using the correct stoichiometric ratio. Suitable crystals of **7** for the X-ray analysis were obtained by slow diffusion of solutions of both reactants in the corresponding solvents. The molecular structure of **7** is shown in Figure 5 and Table 1 collects the most relevant bond parameters.

The complex is tetranuclear, but only half of the molecule is crystallographically independent. The molecule exhibits a C_2 symmetry with an intramolecular crystallographic two-fold axis passing through Ir(2) and Ir(3) atoms. According to this, the four metal atoms conform a strictly-planar almost perfect square, with the metal atoms separated well over 5 Å, and with each iridium atom bonded to the olefinic bonds of two cyclooctene ligands. Each tetradentate iminodicarboxylate ligand is linked to all four metals, with each pair of oxygens of each carboxylate group bridging two contiguous metals, in an alternate way at both sides of the metal square, having an uncoordinated amine group (Figure 5b). All the four metals

exhibit slightly-distorted square-planar environments typical of Ir(I) atoms; it is noteworthy to point out that while the Ir(1) coordination plane is almost coplanar with the tetrametallic square skeleton (dihedral angle 13.26(5)º), those of Ir(2) and Ir(3) are nearly perpendicular (mean 83.57(5)º) to the tetrametallic reference plane.

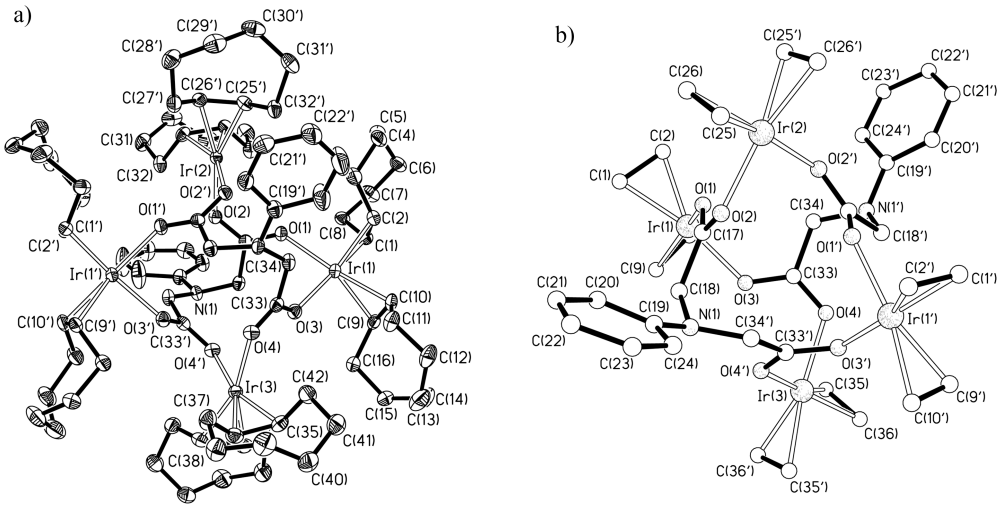


Figure 5. (a) Molecular structure of $[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(coe)_8]$ (**7**). Primed atoms are related to the unprimed ones by the symmetry transformation *1.5-x, 0.5-y, z*. Hydrogen atoms have been omitted for clarity; (b) Schematic drawing showing the κ^4-coordination of each N-phenyliminodicarboxylate group (only the olefinic carbons of the cyclooctene ligands have been represented).

Table 1. Selected bond distances (Å) and angles (º) for the tetranuclear complex $[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(coe)_8]$ (**7**)

Bond distances			
Ir(1)-O(1)	2.105(2)	Ir(1)-O(3)	2.112(2)
Ir(1)-C(1)	2.109(3)	Ir(1)-C(9)	2.096(3)
Ir(1)-C(2)	2.101(3)	Ir(1)-C(10)	2.122(3)
Ir(2)-O(2)	2.105(2)	Ir(3)-O(4)	2.099(2)
Ir(2)-C(25)	2.106(3)	Ir(3)-C(35)	2.120(3)

Ir(2)-C(26)	2.114(3)	Ir(3)-C(36)	2.100(3)
C(1)-C(2)	1.415(5)	C(9)-C(10)	1.407(5)
C(25)-C(26)	1.412(5)	C(35)-C(36)	1.416(5)
Bond angles			
O(1)-Ir(1)-O(3)	85.12(9)	O(3)-Ir(1)-M(1)	172.14(9)
O(1)-Ir(1)-M(1)*	91.08(9)	O(3)-Ir(1)-M(2)*	91.11(9)
O(1)-Ir(1)-M(2)*	173.05(9)	M(1)-Ir(1)-M(2)*	93.35(10)
O(2)-Ir(2)-O(2')	84.54(13)	O(4)-Ir(3)-O(4')	83.59(12)
O(2)-Ir(2)-M(3)*	91.52(10)	O(4)-Ir(3)-M(4)*	92.11(10)
O(2)-Ir(2)-M(3')*	174.47(10)	O(4)-Ir(3)-M(4')*	174.84(10)
M(3)-Ir(2)-M(3')*	92.67(10)	M(4)-Ir(3)-M(4')*	92.31(10)

* M(1), M(2), M(3) and M(4) represent the midpoints of the C(1)-C(2), C(9)-C(10), C(25)-C(26) and C(35)-C(36) olefinic double bonds. Primed atoms are related to the unprimed ones by the symmetry transformation *1.5-x, 0.5-y, z*.

The metal coordination bond distances, Ir-C and Ir-O, show very similar values, with all the figures within very narrow ranges, 2.096-2.122(3) and 2.099-2.112(2) Å respectively, which substantiate the identical electronic nature of all four metals. The Ir-O bond lengths are very similar to those reported in other related carboxylate-bridged dinuclear Ir(I) complexes like $[Ir(\mu\text{-}O_2C_8H_{15})(cod)]_2$ ($O_2C_8H_{15}$ = 2-ethylhexanoate) with a mean value of 2.097(3) Å,[30] or in the polymeric $[IrAg(\mu\text{-}O_2CCF_3)_2(cod)]_n$ where the '$Ir(\mu$-O-carboxylate$)_2$(olefin$)_2$' units are also present (mean 2.095(5) Å).[31] The average olefinic C=C bond length, 1.413(3) Å, compares well with other bis-cyclooctene κ^2-O,O-iridium complexes[32] (mean 1.417(8) Å); this value is clearly longer than the free olefinic double bond C=C (mean 1.316(15) Å)[33] and should be interpreted as the result of the electron rich Ir(I) engaging in a high degree of π-back-bonding.

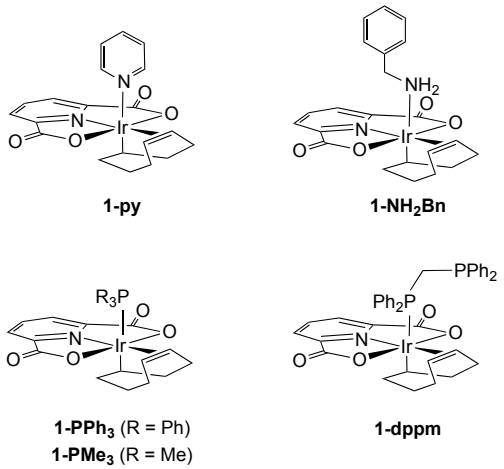
The above described results strongly suggest that the acidity of the dicarboxylic compound is not the only factor that controls the formation of the unsaturated σ,π-cyclooctenyl

iridium(III) complexes. In spite of its weaker Brønsted basicity, the stronger N-coordination ability of the pyridine fragment versus that of the aliphatic amines also should play an important role in the protonation step. In order to test this hypothesis, the reactivity of 2,2'-(pyridine-2,6-diyl)diacetic acid, py(CH_2-COOH)$_2$ (pK_{a1} = 3.08, pK_{a2} = 5.92), was studied.[27] The reaction with standard dinuclear and mononuclear iridium starting materials invariably led to the formation of scarcely soluble yellow solids with poor resolved NMR spectra without any evidenced for the formation of a σ,π-cyclooctenyl iridium(III) complex. Thus, not only the acidity but also the rigidity of the tridentate ligand are determinant factors in the formation of σ-π-cyclooctenyl iridium(III) complexes. As it has been shown before, the key transition state for the proton transfer requires a rigid structure in order to allow the carboxylic group to approach the iridium center. However, in the case of highly flexible tridentate ligands the freedom of the carboxyl group and its fast intermolecular deprotonation by iridium dinuclear complexes probably determines the course of the reaction.

Reactivity of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] with monodentate N- and P-donor ligands. Iridium(III) complexes are usually substitutionally inert, however, the presence of strong labilizing ligands promotes ligand replacement reactions. The *trans* influence exerted by the iridium-alkyl bond in the solvate [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(MeOH)] (**1**·MeOH) points to a labile methanol ligand. Thus, complex **1** can be considered an unsaturated iridium(III) complex and consequently, methanol replacement by more coordinating N- and P-donor ligands could be possible.

Reaction of **1** with an excess of pyridine or benzylamine gave the corresponding complexes [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(py)] (**1-py**) and [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})($BnNH_2$)] (**1-$BnNH_2$**) which were isolated as yellow solids in excellent yields (Scheme 4). Under similar conditions, 2-picoline did not react with **1** probably due to steric constraints. Complexes **1-py** and **1-$BnNH_2$** were fully characterized by spectroscopic means and elemental analysis. The

coordination of the N-donor ligands is confirmed in the ^{1}H NMR spectra where the expected set of resonances for the σ,π-cyclooctenyl ligand was also observed. A characteristic sign for the ligand exchange reaction is the downfield shift by 2-3 ppm of the Ir-*C*H- resonance (C-1) in the ^{13}C{^{1}H} NMR spectra upon the coordination of the N-donor ligands in *trans*.



Scheme 4. Mononuclear complexes derived from **1**.

The molecular structure of **1-py** has been determined by an X-ray analysis and it is shown in Figure 6. The iridium center exhibits a distorted octahedral environment with links to the tridentate meridional *O,N,O*-coordinated pyridinedicarboxylate, to the formally bidentate σ,π-cyclooctenyl ligand and to the nitrogen of the pyridine group. The iridium configuration is such that the olefinic bond is *trans*-situated to the nitrogen of the pydc ligand, while the alkylic cyclooctenyl carbon is also *trans*-positioned to the pyridine group. Major distortions from the octahedral coordination arise from the chelating units within the tridentate pydc group (mean N-Ir-O 78.83(9)º) and, in a minor extension, from the chelating nature of the σ,π-bonded cyclooctenyl ligand (C(11)-Ir-M 84.64(15)º). The pydc ligand is strictly planar and defines a meridional metal coordination plane where the olefin exhibits an in-plane conformation (line-plane angle 1.5(3º)).

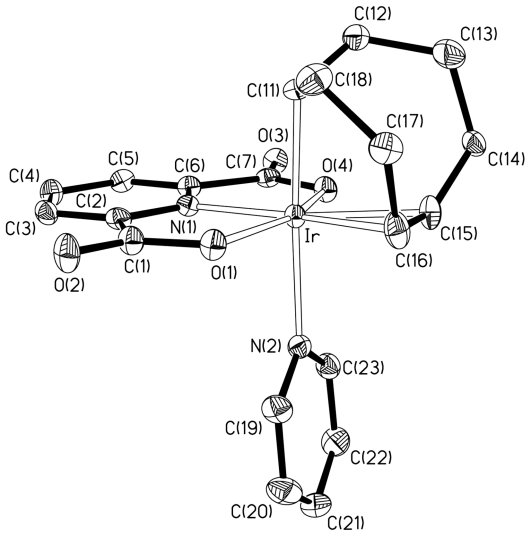


Figure 6. Molecular structure of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(py)] (**1-py**). Bond distances (A) and angles (º) are: Ir-O(1) 2.078(3), Ir-O(4) 2.076(3), Ir-N(1) 1.981(3), Ir-N(2) 2.209(3), Ir-C(11) 2.079(4), Ir-C(15) 2.175(4), Ir-C(16) 2.178(4), C(15)-C(16) 1.373(6); O(1)-Ir-O(4) 157.62(11), O(1)-Ir-N(1) 78.80(12), O(4)-Ir-N(1) 78.86(12), N(1)-Ir-M* 177.02(12), N(2)-Ir-C(11) 176.30(15), C(11)-Ir-M* 84.64(15) (* M represents the midpoint of the olefinic C(15)-C(16) double bond).

The more relevant structural feature of this molecule is the long Ir-N(2) bond length, 2.209(3) Å, a clear consequence of the high structural *trans*-effect of the Ir-alkyl bond. Similar Ir-N bond distances have been observed in Ir(III) complexes where the pyridine molecule is coordinated to the iridium *trans* to a high *trans*-influence ligand: this is the case in [Ir(acac)$_2$R(py)] where R is the cyclohexyl group (Ir-N 2.225(6), Ir-C 2.060(7)),[7c] or a vinyl moiety (Ir-N 2.209(14), Ir-C 1.97(3)),[34] and also when the pyridine group occupies a *trans* position to a hydride ligand ([Ir(PCy_3)($Py)_3H_2$]$^+$ (Ir-N 2.216(2) and 2.2101(19))[35] or to a metal-metal bond such as in [Ir(μ-O_2CCH_3)(CO)Cl(py)]$_2$ (Ir-N 2.200(5)).[36]

Although no iridium structure has been reported including the pincer tridentate pydc ligand, a vast piece of Ir(III) structural chemistry has been described with different substituted derivatives for the *N,O*-bidentate pyridine-2-carboxylate group.[37] It is remarkable that in all

these complexes the Ir-N interaction (2.014-2.215 Å) is surprisingly longer than the distance observed in **1-py** (1.981(3) Å). Additionally, the Ir-O bonds in **1-py** seem also to be stronger (2.078 and 2.076(3) Å) than the usual Ir-O interaction in the bidentate pyridine carboxylate complexes (range 2.033-2.194 Å).[37] Both facts are solid-state evidences of the reported special stabilization associated to the pincer ligands, and particularly for pydc.[11] As a consequence of the commented strong Ir-pydc interaction, and also of the higher oxidation state of the metal atom in **1-py** (compared to that observed in **6**), the Ir-olefin bond seems to be very weak as evidenced by the relative long Ir-C bond lengths (2.175 and 2.178(4) Å) and by the short C=C distance, 1.373(6) Å (weak π-back-donation), only slightly elongated from the ideal value of a free double bond (1.316(15) Å).[33]

Compounds [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(PPh_3)] (**1-PPh$_3$**) and [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(PMe_3)] (**1-PMe$_3$**) (Scheme 4) were prepared by reacting **1** with one equiv. of the corresponding phosphine ligand and isolated as lemon yellow solids in excellent yields. The $^{31}P\{^1H\}$ NMR of the complexes showed the expected singlet resonances at -7.23 (**1-PPh$_3$**) and -38.98 ppm (**1-PMe$_3$**). In addition, the coordination of the PR_3 ligands *trans* to the iridium-alkyl bond of the cyclooctenyl ligand is supported by the large $J_{C\text{-}P}$ coupling of the Ir-*C*H- resonance (C-1) in the $^{13}C\{^1H\}$ NMR spectra, which was observed at 31.72 ($J_{C\text{-}P}$ = 85.8 Hz) and 31.29 ppm ($J_{C\text{-}P}$ = 91.5 Hz), respectively. It is noticeable that an excess of PR_3 does not induce the decoordination neither of the σ,π-cyclooctenyl nor the pincer ligands, which demonstrate the outstanding stability of the rigid molecular framework in **1**.

Reactivity of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] with bidentate P-donor ligands. In order to induce a possible change in the coordination mode of the σ,π-cyclooctenyl moiety in [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**) we have explored its reactivity with chelating diphosphines. Reaction of **1** with one equiv. of bis(diphenylphosphino)methane (dppm) gave [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(κ^1-dppm)] (**1-dppm**) which features a monocoordinated dppm ligand

(Scheme 4). The compound, which was obtained as a lemon yellow solid in 87% yield, has been fully characterized in solution by spectroscopic methods and in the solid state by a single crystal X-ray analysis. The presence of a κ^1-dppm coordinated ligand became evident in the $^{31}P\{^1H\}$ NMR spectrum that showed two strong coupled doublet resonances at -17.47 and -27.81 ppm ($J_{P\text{-}P}$ = 70.7 Hz) corresponding to the coordinated and uncoordinated P donor atoms, respectively.[38] On the other hand, the coordination of the dppm ligand *trans* to the Ir-*C*H- bond of the σ,π-cyclooctenyl ligand was derived from the large $J_{C\text{-}P}$ coupling of 86.2 Hz observed for the C-1 resonance at 31.57 ppm in the $^{13}C\{^1H\}$ NMR spectrum. In addition, the >*C*H_2 resonance of the dppm ligand was observed as a doublets of doublets at 23.96 ppm with $J_{C\text{-}P}$ couplings of 31.2 and 16.7 Hz.

The molecular structure of **1-dppm** is shown in Figure 7. This molecule resembles quite well that of **1-py** in which the pyridine group has been substituted by a monodentate P-bonded dppm ligand. The complex exhibits an analogous octahedral coordination, with the same stereo-distribution of ligands and statically identical molecular parameters for the pydc and for the σ,π-bonded cyclooctenyl ligands. Only the Ir-C bond distances of the coordinated olefinic group are significantly longer (mean 2.215(6) Å in **1-dppm**) than those observed in **1-py** (2.176(3) Å), although the C=C bond distance does not vary accordingly (1.387(13) *vs*. 1.373(6) Å).

A remarkable difference of this molecule if compared with **1-py** is the deviation of the olefinic carbons from the strictly-planar meridional plane described by the three donor atoms of the pyridinedicarboxylate group and the metal atom; while in **1-py** the olefin fits reasonable in this plane (N-Ir-M 177.02(12)º), in **1-dppm** the olefin is clearly out of this plane by a mean value of 0.322(8) Å, with a closer N-Ir-M bond angle of 171.3(3)º. Most probably this fact should be associated to the bulkier character of dppm compared to pyridine.

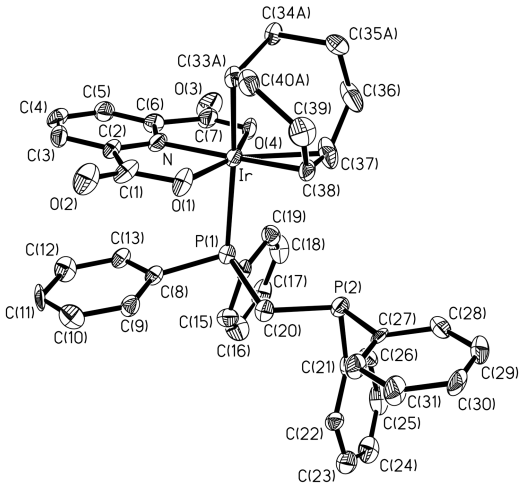


Figure 7. Molecular structure of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(κ^1-dppm)] (**1-dppm**). Bond distances (A) and angles (º) are: Ir-O(1) 2.074(6), Ir-O(4) 2.057(6), Ir-N(1) 1.975(6), Ir-P(1) 2.458(2), Ir-C(33A)$^{\#}$ 2.108(14), Ir-C(37) 2.225(9), Ir-C(38) 2.204(8), C(37)-C(38) 1.387(13); O(1)-Ir-O(4) 157.1(2), O(1)-Ir-N(1) 78.3(3), O(4)-Ir-N(1) 78.8(3), N(1)-Ir-M* 171.3(3), P(1)-Ir-C(33A)$^{\#}$ 167.6(5), C(33A)-Ir-M* 81.7(5) (*M represents the midpoint of the olefinic C(37)-C(38) double bond; $^{\#}$Bond parameters involving C(33) are only expressed for the disordered carbon atom of higher occupancy).

As commented for the pyridine in **1-py**, the high structural *trans*-effect of the alkylic Ir-C bond elongates the Ir-P(1) bond length to a value of 2.458(2) Å. As far as we know, this is the longest Ir-P bond distance observed in a Ir(III) complex containing a PR_3 phosphine *trans*-situated (C-Ir-P > 160º) to an alkylic sp^3 carbon (range 2.276-2.410 Å, mean 2.343(2) Å).[37] If the metal complex should contain a dppm ligand, the longest Ir-P separation (*trans* to an alkylic carbon) described so far is 2.382(1) in [$IrMe_2(dppm)_2$][OTf].[39] All these facts evidence a weak bonding interaction between the metal and the monodentate diphosphine.

Reaction of **1** with one equiv. of 1,2-bis(diphenylphosphino)ethane (dppe) gave a yellow solid that consists of roughly a 1:1 mixture of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(κ^1-dppe)] (**1-dppe**) and the dinuclear compound [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})]$_2$(μ-dppe) (**1_2-dppe**) having

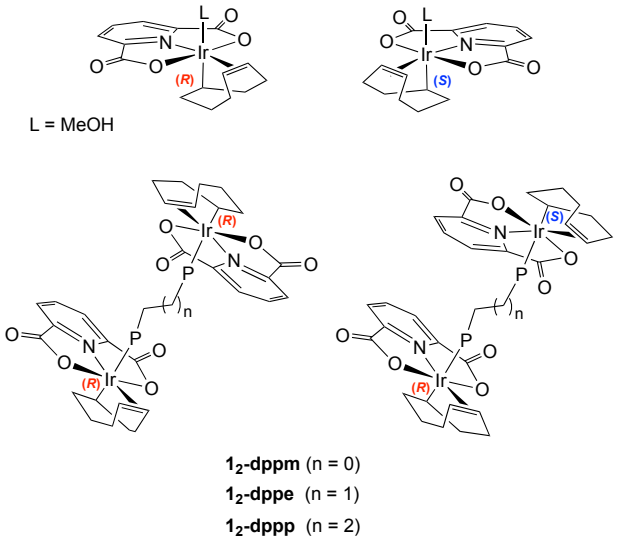
a dppe ligand bridging two [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] fragments (Scheme 5). The $^{31}P\{^1H\}$ NMR (121.49 MHz) spectrum of this mixture in CD_2Cl_2 at room temperature showed a set of three broad resonances suggesting a fluxional behavior. However, the spectrum at 223 K featured well-defined resonances. The two coupled resonances at -12.12 and -14.17 ppm ($J_{P\text{-}P}$ = 32 Hz) were assigned to **1-dppe**, and the two signals at -10.89 and -11.09 ppm to the two diastereoisomers of **1_2-dppe** (see below). Most probably, both species are in a dppe-mediated dynamic equilibrium[40] that causes resonances to broaden at room temperature.

$$2\ \textbf{1-dppe} \ \leftrightarrows\ \textbf{1}_2\textbf{-dppe} + \text{dppe}$$

The dinuclear complex **1_2-dppm** has been isolated from the solution obtained after dissolving a solid mixture of **1** and half equiv. of dppm in CH_2Cl_2/MeOH (3/1). This method has revealed also useful for the synthesis of compounds **1_2-dppe** and **1_2-dppp** using the corresponding diphosphines. The complexes have been obtained as yellow solids in yields over 80% and fully characterized by elemental analysis, mass spectra and multinuclear NMR spectroscopy. The ESI spectra of the three compounds showed the molecular ions of the mononuclear complexes [**1-diphos**]$^+$ resulting from the loss of one of the iridium fragments. However, the ESI spectrum of **1_2-dppe** showed the molecular ion at *m/z* 1329.2 with the right isotopic distribution.

The C-1 atom of the σ-π cyclooctenyl ligand in **1** is a stereogenic center and then, compound **1** is chiral and exists as a pair of enantiomers, namely (R_C)-(**1**) and (S_C)-(**1**). The assembly of the dinuclear compounds **1_2-(μ-diphos)** can produce three stereoisomers: the enantiomeric pair [(R_C)-(**1**)]$_2$(μ-diphos)/[(S_C)-(**1**)]$_2$(μ-diphos) (indistinguishable by NMR) and [(R_C)-(**1**)][(S_C)-(**1**)](μ-diphos), with C_2 and C_s symmetries, respectively (Scheme 5). As expected, the dinuclear compounds exist as a 1:1 mixture of both diastereoisomers which have been observed in the $^{31}P\{^1H\}$ NMR spectra as two single resonances (see Experimental

Section). In addition, the C-1 resonances of the equivalent σ,π-cyclooctenyl ligands in both diastereoisomers of **1_2-dppe** were observed as doublet of doublets at 32.55 and 32.41 ppm in the $^{13}C\{^1H\}$ NMR spectrum with $J_{C\text{-}P}$ coupling constants of 90.0 and 2.2 Hz which further supports the proposed structure.



Scheme 5. Dinuclear complexes derived from **1**.

Conclusions

The synthesis of the unusual σ,π-cyclooctenyl iridium (III) pincer compounds [Ir(κ^3-pydc-X)(1-κ-4,5-η-C_8H_{13})] can be accomplished by several routes involving the corresponding 4-substituted 2,6-pyridinedicarboxylic acids or their lithium salts, and standard mono- or dinuclear iridium complexes. The investigation of the mechanism of the reaction have shown the initial formation of the species [Ir(κ^2-Hpydc)(cod)] having a monodeprotonated ligand κ^2-*N,O* coordinated. Deuterium labeling studies in combination with theoretical calculations at DFT level have shown that the formation of the σ,π-cyclooctenyl iridium (III) complexes involves a metal-mediated proton transfer to the 1,5-cyclooctadiene ligand through an methanol-stabilized hydrido species [IrH(κ^2-pydc)(cod)(CH_3OH)]. Remarkably, the

formation of this key hydrido intermediate results from the solvent-assisted proton transfer through a hydrogen-bonding network involving a carboxyl group, a methanol molecule and the iridium center forming an eight-membered metallacycle.

The application of this synthetic methodology with related dicarboxylic acids precursors for dianionic tridentate pincer ONO complexes has shown a narrow scope. However, the reactivity of some iminodiacetic acids derivatives, $RN(CH_2COOH)_2$ (R = Me, Ph), has allowed us to identify the acidity (pK_a) and the rigidity of the potential tridentate ligand precursor as the key factors leading σ,π-cyclooctenyl iridium(III) complexes.

Complex [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] behaves as an unsaturated species and coordination of some monodentate N- and P- donor ligands has lead for the preparation of octahedral complexes. The stability of the rigid molecular framework has allowed for the preparation of diphosphine-bridged dinuclear assemblies that have been obtained as a mixture of two diastereoisomers. Interestingly, in the case of the short-bite bis(diphenylphosphino)methane ligand the nuclearity can be modulated and a mononuclear complex having a κ^1-dppm ligand has been also prepared.

Experimental Section

General considerations: All experiments were carried out under an atmosphere of argon using Schlenk techniques or glovebox. Solvents were obtained from a Solvent Purification System (Innovative Technologies). CD_2Cl_2 and DMSO-d^6 (Euriso-top) were dried using activated molecular sieves. Methanol-d^4 (<0.02% D_2O, Euriso-top) was used as received. Elemental analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. NMR spectra were recorded on Bruker AV-400 and AV-300 spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in Hertz. Spectral assignments were achieved by

combination of ^{1}H-^{1}H COSY, ^{13}C DEPT, APT, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The numbering scheme used in the NMR data of the compounds is shown in Figure 1. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formiate as reference. MALDI-Tof mass spectra were obtained on a Bruker Microflex mass spectrometer using DCTB (*trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) or dithranol as matrix. Standard literature procedures were used to prepare the starting materials $[Ir(\mu\text{-}OMe)(cod)]_2$,[41] $[Ir(\mu\text{-}OH)(coe)_2]_2$,[42] and $[Ir(cod)(NCCH_3)_2]PF_6$.[43] Pyridine-2,6-dicarboxylic acid (H_2pydc), N-methyliminodiacetic and N-phenyliminodiacetic acids were obtained from Fluka, Aldrich and Acros, respectively, and used as received. 4-bromopyridine-2,6-dicarboxylic acid (Hpydc-Br) was prepared from chelidamic acid (4-hydroxypyridine-2,6-dicarboxylic acid, Fluka) following the procedure described in the literature.[44]

Lithium pyridine-2,6-dicarboxylate (Li_2pydc). To a suspension of 2,6-pyridinedicarboxylic acid (0.268 g, 1.60 mmol) in diethyl ether (20 mL) was added dropwise a 1.6 M solution of *n*-BuLi in hexane (2.0 mL, 3.2 mmol) while stirring at 195 K. The reaction mixture was warmed to room temperature within 1h. During this time, the colour of the suspension turned from white to pale yellow. The resulting suspension was concentrated, decanted and filtered to afford an off-white solid, which was washed with diethyl ether (3x10 mL) and dried *in vacuo*. Yield: 0.279 g (97 %). ^{1}H NMR (400.16 MHz, 298 K, DMSO-d^6): δ 8.24 (m, 2H), 8.18 (m, 1H).

Lithium 6-carboxypicolinate (HLipydc). 2,6-pyridinedicarboxylic acid (0.268 g, 1.60 mmol) and *n*-BuLi in hexane (1.0 mL, 1.6 mmol) were reacted in diethyl ether (20 mL) at 195 K. Work up as described above gave the salt as an off-white solid. Yield: 0.263 g (95 %). ^{1}H NMR (400.16 MHz, 298 K, DMSO-d^6): δ 13.38 (br, 1H, -COOH), 8.23 (m, 2H), 8.17 (m, 1H).

[Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)] (1). *Method A*. [Ir(μ-OMe)(cod)]$_2$ (0.132 g, 0.200 mmol) and H$_2$pydc (0.068 g, 0.40 mmol) were reacted in a CH_2Cl_2/MeOH mixture (3/1, 20 mL) for 14 h to give a bright yellow solution. The solution was brought to dryness *in vacuo* and the crude compound dissolved in a CH_2Cl_2/MeOH (20:1) mixture (2 mL) and then eluted through an alumina column (5 x 1.5 cm) to give a yellow solution. Concentration of the solution to ca. 1 mL and slow addition of diethyl ether gave the compound as a yellow solid which was filtered, washed with diethyl ether (2 x 3 mL) and dried *in vacuo*. Yield: 0.170 g (85%). *Method B*. A solid mixture of [Ir(cod)(CH$_3$CN)$_2$]PF$_6$ (0.106 g, 0.200 mmol) and LiHpydc (0.035 g, 0.200 mmol) was dissolved in a CH_2Cl_2/MeOH mixture (3/1, 20 mL). The resulting red solution was stirred for 14 h to give a bright yellow solution. The solution was filtered and then concentrated under vacuum to ca. 5 mL. Slow addition of diethyl ether (20 mL) gave the compound as a yellow solid that was filtered, washed with diethyl ether and dried under vacuum. Yield: 0.096 g (96%). *Method C*. [Ir(cod)(CH$_3$CN)$_2$]PF$_6$ (0.106 g, 0.200 mmol) and Li$_2$pydc (0.036 g, 0.200 mmol) were reacted in a CH_2Cl_2/MeOH mixture (3/1, 20 mL) for 14 h to give a bright yellow solution. Work up as described above (Method B) afforded the compound as a yellow solid. Yield: 0.090 g (90%). The analytic and spectroscopic data evidenced that compound **1** was actually isolated as the methanol solvate **1**·MeOH.[11] Found: C, 38.42; H, 3.98; N, 2.75. Calc. for C$_{15}$H$_{16}$IrNO$_4$·CH$_3$OH: C, 38.54; H, 4.04; N, 2.81 (*Method B*).

[Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{12}$D)] (1-*d*^{1}). A solid mixture of [Ir(cod)(CH$_3$CN)$_2$]PF$_6$ (0.053 g, 0.10 mmol) and [Li$_2$pydc] (0.018 g, 0.10 mmol) was dissolved in CD_2Cl_2/CD_3OD/D_2O (4.2 mL, 3/1/0.1, respectively). The solution stirred at room temperature for 14 h and then directly analyzed by NMR. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2/CD_3OD): δ 8.35 (t, $J_{H\text{-}H}$ = 7.8 Hz, 1H, 4-H), 8.18 (dd, $J_{H\text{-}H}$ = 7.8 and 1.2 Hz, 1H, 3-H or 5-H), 8.12 (dd, $J_{H\text{-}H}$ = 7.8 and 1.2 Hz, 1H, 3-H or 5-H) (pydc), 5.81 (dt, $J_{H\text{-}H}$ = 9.1 and 3.0 Hz, 1H, 4-H), 5.59 (d, $J_{H\text{-}H}$ = 9.9 Hz, 1H,

5-H), 3.13 (d, J_{H-H} = 15.9 Hz, 1H, 6-H), 2.35 (m, J_{H-H} = 11.0 and 4.3 Hz, 1H, 3-H), 2.29-2.13 (bm, 2H, 3-H and 6-H), 2.01-1.82 (bm, 3H, 1-H, 2-H and 7-H), 1.59 (bd, J_{H-H} = 14.1 Hz, 1H, 7-H), 0.39 (dd, J_{H-H} = 12.3 and 3.6 Hz, 1H, 2-H), 0.01 ppm (d, J_{H-H} = 3.3 Hz, 1H, 8-H) ($C_8H_{12}D$). $^{13}C\{^1H\}$ NMR (75.48 MHz, 298 K, CD_2Cl_2/CD_3OD): δ 175.55, 175.22 (*C*O), 148.31, 147.17 (C-2 and C-6), 141.30 (C4) (pydc), 89.53 (C-4), 85.08 (C-5), 40.69 (C-2), 34.73 (t, J_{C-D} = 19.0 Hz, C-8), 27.83 (C-6), 26.29 (C-3), 25.07 (C-7), 15.09 (C-1) (1-κ-4,5-η-$C_8H_{12}D$). ^2H NMR (61.42 MHz, 298 K, CH_2Cl_2/MeOH): δ 1.21 (s, 1D, $C_8H_{12}D$). MS (MALDI-Tof, DCTB, CH_2Cl_2/MeOH) *m/z*: 467.9 (M^+), 316.4 (M^+- pydc).

[Ir(κ^3-pydc-Br)(1-κ-4,5-η-C_8H_{13})] (3). H_2pydc-Br (0.246 g, 1.00 mmol) and [Ir(μ-OMe)(cod)]$_2$ (0.331 g, 0.500 mmol) were reacted in CH_2Cl_2/MeOH (40 mL, 5:1) for 14 h at room temperature to give a red solution. Work up as described above for **1** (*Method A*) gave the compound as red solid. Yield: 0.532 g (94%). Found: C, 32.05; H, 2.92; N, 2.53. Calc. for $C_{15}H_{15}BrIrNO_4{\cdot}H_2O$: C, 31.98; H, 3.04; N, 2.49. ^1H NMR (400.16 MHz, 298 K, CD_2Cl_2/CD_3OD): δ 8.28 (s, 1H), 8.24 (s, 1H) (3-H and 5-H, pydc-Br), 5.87 (td, J_{H-H} = 8.8 and 3.7 Hz, 1H, 4-H), 5.64 (br, 1H, 5-H), 3.17 (d, J_{H-H} = 15.9 Hz, 1H, 6-H) 2.40-2.10 (m, 3H, 3-H and 6-H), 2.01 (m, 1H, 1-H), 1.97 (d, J_{H-H} = 9.4 Hz, 1H, 2-H), 1.85 (dt, J_{H-H} = 14.1 and 4.6 Hz, 1H, 7-H), 1.63 (t, J_{H-H} = 6.08 Hz, 1H, 7-H), 0.94 (tt, J_{H-H} = 14.6 and 2.4 Hz, 1H, 8-H), 0.40 (dd, J_{H-H} = 14.2 and 9.22, 1H, 2-H), 0.03 (dm, J_{H-H} = 13.8 Hz, 1H, 8-H) (C_8H_{13}). $^{13}C\{^1H\}$ NMR (75.48 MHz; 298 K; CD_2Cl_2/CD_3OD): δ 172.8 (*C*O), 147.7, 146.6 (C-2 and C-6), 133.1, 132.8 (C-3 and C-5), 135.6 (C-4) (pydc-Br), 89.0 (C-4), 85.0 (C-5), 39.6 (C-2), 34.1 (C-8), 26.8 (C-6), 25.3 (C-3), 24.0 (C-7), 14.6 (C-1) (C_8H_{13}). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 527.2 (M^+).

[Ir{κ^2-MeN(CH_2COOH)(CH_2COO)}(cod)] (5). A solid mixture of [Ir(μ-OMe)(cod)]$_2$ (0.041 g, 0.062 mmol) and N-methyliminodiacetic acid (0.018 g, 0.124 mmol) was dissolved in THF (15 ml) and the solution stirred for 3 h at 50 °C. The solvent was removed under

vacuum and the orange residue washed with hexane (2 x 2 ml) and then dried *in vacuo*. Yield: 0.047 g (85%). ^{1}H NMR (400.16 MHz, CD_2Cl_2/CD_3OD, 298 K): δ 5.00 (m, 1H), 4.85 (m, 1H), 4.63 (m, 1H), 4.32 (m, 1H) (=CH, cod), 3.83 (AB q, 2H, $\delta_A = 3.90$, $\delta_B = 3.76$, J_{AB} = 16.1 Hz, J_{AC} = 1.8 Hz, $>CH_2$), 3.68 (CD q, 2H, $\delta_C = 3.79$, $\delta_D = 3.56$, J_{CD} = 16.6 Hz, J_{AC} = 1.8 Hz, $>CH_2$), 2.89 (s, 3H, $-CH_3$), 2.80-2.67 (m, 2H), 2.64-2.55 (m, 2H), 2.46 (m, 1H), 2.23 (m, 1H), 1.91 (m, 1H), 1.56 (m, 1H) ($>CH_2$, cod). ^{13}C{^{1}H} NMR (75.48 MHz, CD_2Cl_2/CD_3OD, 298 K): δ 181.3, 180.4 (*C*O), 87.1, 82.9, 77.7, 76.4 (=CH, cod), 71.2 ($>CH_2$), 69.0 ($>CH_2$), 56.4 ($-CH_3$), 34.7, 31.5, 30.2, 26.1 ($>CH_2$, cod).

$[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(cod)_4]$ (6). A solution of N-phenyliminodiacetic acid (0.035 g, 0.167 mmol) in methanol (3 mL) was added to a solution of $[Ir(\mu\text{-}OMe)(cod)]_2$ (0.111 g, 0.167 mmol) in dichloromethane (3 mL) to give a red solid in one minute. The solution was decanted and the solid washed with methanol (2 x 3 mL) and dried under vacuum. Yield: 0.108 g (80%). Found: C, 38.46; H, 4.10; N, 1.76. Calc. for $C_{52}H_{66}Ir_4N_2O_8$: C, 38.65; H, 4.12; N, 1.73.

$[Ir_4\{\kappa^4\text{-}PhN(CH_2COO)_2\}_2(coe)_8]$ (7). A solution of N-phenyliminodiacetic acid (0.014 g, 0.068 mmol) in methanol (2 mL) was added to a solution of $[Ir(\mu\text{-}OH)(coe)_2]_2$ (0.058 g, 0.068 mmol) in dichloromethane (2 mL). After one minute a yellow/orange solid precipitated from the solution. The solution was decanted and the solid washed with methanol (2 x 3 mL) and dried under vacuum. Yield: 0.066 g (90%). Found: C, 48.86; H, 6.35; N, 1.35. Calc. for $C_{84}H_{130}Ir_4N_2O_8{\cdot}2CH_3OH$: C, 48.51; H, 6.53; N, 1.32. Suitable crystals for X-ray diffraction were obtained by layering a solution of $[Ir(\mu\text{-}OH)(coe)_2]_2$ in dichloromethane over a solution of N-phenyliminodiacetic acid in methanol at room temperature.

$[Ir(\kappa^3\text{-}pydc)(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})(py)]$ (1-py). The compound was prepared by refluxing a solution of $[Ir(\kappa^3\text{-}pydc)(1\text{-}\kappa\text{-}4,5\text{-}\eta\text{-}C_8H_{13})]$ (**1**) in net pyridine and isolated as a yellow solid in

85% yield.[11] Good quality microcrystals for X-ray diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution of **1-py** at 258 K.

[Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)(BnNH$_2$)] (1-BnNH$_2$). Benzylamine (2 mL) was added to a suspension of [Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)] (**1**·MeOH) (0.100 g, 0.200 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was heated at 90°C for 3h with stirring to give a yellow solution. The solution was cooled to room temperature and evaporated to dryness *in vacuo*. Crystallization from CH_2Cl_2/Et_2O at low temperature afforded the compound as lemon yellow microcrystals. Yield: 0.100 g (87%). Found: C, 46.23; H, 4.54; N, 4.95. Calc. for $C_{22}H_{25}IrN_2O_4$: C, 46.06; H, 4.39; N, 4.88. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 8.08 (t, 1H, $J_{H\text{-}H}$ = 8.0 Hz, 4-H), 7.96 (dd, 1H, $J_{H\text{-}H}$ = 7.3 and 1.6 Hz), 7.88 (dd, 1H, $J_{H\text{-}H}$ = 7.3 and 1.6 Hz) (3-H and 5-H) (pydc), 7.32-7.22 (m, 4H, -NH_2 and Bn), 7.06 (m, 2H, Bn), 6.93 (m, 1H, Bn) ($BnNH_2$), 5.76 (td, 1H, $J_{H\text{-}H}$ = 9.5 and 3.6 Hz, 4-H), 5.41 (d, 1H, $J_{H\text{-}H}$ = 8.0 Hz, 5-H) (C_8H_{13}), 3.18 (m, 2H, >CH_2, Bn), 3.02 (d, 1H, $J_{H\text{-}H}$ = 16.1 Hz), 2.35 (m, 1H), 2.14-2.03 (m, 2H), 1.88-1.73 (m, 2H), 1.50 (d, 1H, $J_{H\text{-}H}$ = 13.2 Hz), 1.37 (m, 1H), 0.89 (t, 1H, $J_{H\text{-}H}$ = 13.9 Hz), 0.60 (dd, 1H, $J_{H\text{-}H}$ = 13.2 and 9.2 Hz), 0.27 (m, 1H) (C_8H_{13}). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, CD_2Cl_2): δ 176.36, 176.06 (*C*O), 148.48, 147.46 (C-2 and C-6) (pydc), 141.44 (Bn), 140.83 (C-4), 132.07, 131.72 (C-3 and C-5) (pydc), 131.36 (C_m), 121.27 (C_p), 130.95 (C_o) (Bn), 90.20 (C-4), 85.72 (C-5) (pydc), 45.89 (>CH_2, Bn), 41.39 (C-2), 35.47 (C-8), 28.80 (C-6), 28.64 (C-3), 25.94 (C-7), 18.82 (C-1) (C_8H_{13}). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m*/*z*: 467.9 (M^+ - $BnNH_2$).

[Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)(PR$_3$)]. A solid mixture of [Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)] (**1**·MeOH) (0.100 g, 0.200 mmol) and the corresponding PR_3 (0.200 mmol) was dissolved in CH_2Cl_2/MeOH (3/1, 10 mL) and the solution stirred at room temperature for 14 h. The resulting solution was evaporated to dryness. The residue was subsequently dissolved in a minimum volume of dichloromethane and then diethyl ether was poured to give the

compounds as lemon yellow solids which were filtered, washed with diethyl ether (3 x 10 mL) and dried under vacuum.

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(PPh_3)] (1-PPh_3). Yield: 0.137 g (96%). Found: C, 54.47; H, 4.32; N 1.98. Calc. for $C_{33}H_{31}IrNO_4P$: C, 54.38; H, 4.29; N 1.92. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 7.81 (t, 1H, J_{H-H} = 8.2 Hz, 4-H), 7.66 (dd, 1H, J_{H-H} = 7.8 and 1.2 Hz), 7.57 (dd, 1H, J_{H-H} = 7.8 and 1.2 Hz) (3-H and 5-H) (pydc), 7.32 (tq, 3H, J_{H-H} = 7.3 and 1.5 Hz), 7.21 (td, 6H, J_{H-H} = 7.3 and 2.0 Hz), 7.13 (tt, 6H, J_{H-H} = 8.3 and 1.3 Hz) (PPh_3), 5.70 (t, 1H, J_{H-H} = 6.8 Hz, 4-H), 5.61 (t, 1H, J_{H-H} = 8.6 Hz, 5-H), 2.95 (d, 1H, J_{H-H} = 16.9 Hz, 6-H), 2.35-2.48 (m, 1H, 3-H), 2.20-2.30 (m, 2H, 3-H and 6-H), 2.11 (m, 1H, 2-H), 1.84 (dtt, 1H, J_{H-H} = 18.1, 13.9 and 4.3 Hz, 7-H), 1.59 (d, 1H, J_{H-H} = 13.9 Hz, 7-H), 1.46 (q, 1H, J_{H-H} = 3.3 Hz, 1-H), 1.34 (td, 1H, J_{H-H} = 3.3 and 13.9 Hz, 8-H), 0.89 (m, 1H, 2-H), 0.65 (m, 1H, 8-H) (C_8H_{13}). ^{13}C{^{1}H} NMR (75.479 MHz, 298 K, CD_2Cl_2): δ 172.07, 171.48 (*C*O), 145.81, 144.63 (C-2 and C-6), 137.56 (C-4) (pydc), 133.77 (d, J_{C-P} = 10.5 Hz, C_o), 130.47 (C_p) (PPh_3), 129.40, 129.10 (C-3 and C-5, pydc), 128.82 (d, J_{C-P} = 8.9 Hz, C_m), 128.63 (d, J_{C-P} = 60.0 Hz, C_{ipso}) (PPh_3), 90.67 (C-4), 82.15 (C-5), 37.59 (d, J_{C-P} = 3.8 Hz), 32.46 (d, J_{C-P} = 3.4 Hz) (C-2 and C-8), 31.72 (d, J_{C-P} = 85.8 Hz, C-1), 27.33 (d, J_{C-P} = 7.2 Hz, C-7), 26.11, 23.39 (C-3 and C-6) (C_8H_{13}). ^{31}P{^{1}H} NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -7.23 (s). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 467.9 (M^+ - PPh_3).

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(PMe_3)] (1-PMe_3). Yield: 0.098 g (90%). Found: C, 39.74; H, 4.69; N, 2.54. Calc. for $C_{18}H_{25}IrNO_4P$: C, 39.84; H, 4.64; N 2.58. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 8.07 (t, 1H, J_{H-H} = 7.5 Hz, 4-H), 8.02 (dd, 1H, J_{H-H} = 9.4 and 1.4 Hz), 7.97 (dd, 1H, J_{H-H} = 9.4 and 1.4 Hz) (3-H and 5-H) (pydc), 5.86 (t, 1H, J_{H-H} = 8.8 Hz, 4-H), 5.55 (t, 1H, J_{H-H} = 8.8 Hz, 5-H), 3.00 (d, 1H, J_{H-H} = 16.9 Hz), 2.53 (m, 1H), 2.25 (m, 1H), 2.15-1.97 (m, 2H), 1.83 (dtt, 1H, J_{H-H} = 13.9, 18.3 and 3.7 Hz), 1.56 (m, 1H), 1.29-1.15 (m, 2H), 0.97 (m, 1H) (C_8H_{13}), 0.87 (d, 9H, J_{H-P} = 14.3 Hz, PMe_3), 0.79 (m, 1H, C_8H_{13}). ^{13}C{^{1}H} NMR

(100.62 MHz, 298 K, CD_2Cl_2): δ 172.58 (d, J_{C-P} = 2.2 Hz), 172.05 (d, J_{C-P} = 2.9 Hz) (*C*O), 146.09, 145.13 (C-2 and C-6), 138.34 (d, J_{C-P} = 2.2 Hz, C-4), 129.82 (d, J_{C-P} = 2.2 Hz), 129.46 (t, *J* = 2.9 Hz) (C-3 and C-5) (pydc), 87.93 (d, J_{C-P} = 1.5 Hz, C-4), 82.44 (C-5), 37.17 (d, J_{C-P} = 4.4 Hz), 32.54 (d, J_{C-P} = 3.7 Hz) (C-2 and C-8), 31.29 (d, J_{C-P} = 91.5 Hz, C-1), 28.42 (d, J_{C-P} = 8.1 Hz, C-7), 26.64, 23.83 (C-3 and C-6) (C_8H_{13}), 9.46 (d, *J* = 22.0 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -38.98 (s). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 467.9 (M^+ - PMe_3).

[Ir(κ^3-pydc)(1-κ-4,5-η-C$_8$H$_{13}$)(κ^1-dppm)] (1-dppm): A solution of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**·MeOH) (0.100 g, 0.200 mmol) in CH_2Cl_2/MeOH (3/1, 10 mL) was slowly cannuled to a solution of dppm (0.077 g, 0.20 mmol) in CH_2Cl_2 (5 mL).The reaction mixture was stirred at room temperature for 14 h and then evaporated to dryness. The residue was dissolved in the minimum volume of dichloromethane and then diethyl ether was poured to give a lemon yellow solid, which was filtered, washed with diethyl ether (3 x 10 mL) and dried under vacuum. Yield 0.148 g (87%). Crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution of **1-dppm** at 258 K. Found C, 56.62; H, 4.32; N, 1.42. Calc. for $C_{40}H_{38}IrNO_4P_2$: C, 56.46; H, 4.50; N, 1.65. ^1H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 7.65 (td, 1H, J_{H-H} = 7.7 and 1.3 Hz, 4-H), 7.58 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz), 7.45 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz) (3-H and 5-H) (pydc), 7.19-7.04 (m, 14H, Ph), 6.99 (m, 2H, Ph), 6.91 (m, 2H, Ph), 6.84 (m, 2H, Ph) (dppm), 6.43 (t, 1H, J_{H-H} = 7.8 Hz, 4-H), 6.16 (t, 1H, J_{H-H} = 8.6 Hz, 5-H), 3.06 (d, 1H, J_{H-H} = 20.0 Hz) (C_8H_{13}), 3.02 (d, 2H, J_{H-H} = 6.8 Hz, >CH_2, dppm), 2.48 (m, 1H), 2.30-2.18 (m, 2H), 2.05 (m, 1H), 1.87 (m, 1H), 1.61 (d, 1H, J_{H-H} = 14.9 Hz), 1.38-1.25 (bm, 2H), 0.88 (m, 1H), 0.65 (m, 1H) (C_8H_{13}). $^{13}C\{^1H\}$ NMR (75.479 MHz, 298 K, CD_2Cl_2): δ 172.30, 171.58 (*C*O), 145.74 (d, J_{C-P} = 1.6 Hz), 144.30 (d, J_{C-P} = 1.6 Hz) (C-2 and C-6) (pydc), 138.12 (d, J_{C-P} = 32.6 Hz), 138.04 (d, J_{C-P} = 31.2 Hz), 137.94 (d, J_{C-P} = 32.4 Hz), 137.85 (d, J_{C-P} = 30.9 Hz) (C_{ipso}, dppm), 137.15 (d, J_{C-P}

= 1.6 Hz, C-4) (pydc), 133.72 (d, J_{C-P} = 10.3 Hz), 133.70 (d, J_{C-P} = 10.4 Hz), 133.07, 132.78, 132.40, 132.27 (d, J_{C-P} = 10.0 Hz), 132.26 (d, J_{C-P} = 9.9 Hz), 132.13 (dppm), 130.44 (d, J_{C-P} = 2.0 Hz), 129.60 (d, J_{C-P} = 2.0 Hz) (C-3 and C-5) (pydc), 129.05, 128.68, 128.56 (d, J_{C-P} = 7.8 Hz), 128.55, 128.40 (d, J_{C-P} = 8.3 Hz), 128.39 (d, J_{C-P} = 8.5 Hz), 128.23 (dppm), 89.64 (d, J_{C-P} = 6.7 Hz, C-4), 81.72 (d, J_{C-P} = 7.8 Hz, C-5) (pydc), 37.09 (d, J_{C-P} = 5.9 Hz), 32.24 (d, J_{C-P} = 3.3 Hz) (C-2 and C-8), 31.57 (d, J_{C-P} = 86.2 Hz, C-1), 27.55 (d, J_{C-P} = 7.3 Hz, C-7), 26.07 (C-3 or C-6) (C_8H_{13}), 23.96 (dd, J_{C-P} = 31.2 and 16.7 Hz, >*C*H_2, dppm), 23.66 (C-3 or C-6) (C_8H_{13}). $^{31}P\{^1H\}$ NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -17.47 (d, J_{P-P} = 70.7 Hz), -27.81 (d, J_{P-P} = 70.7 Hz). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 961.2 [$Ir(dppm)_2^+$], 684.1 (M^+ - pydc).

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})]$_2$(μ-diphosphine): A solid mixture of [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})] (**1**·MeOH) (0.100 g, 0.200 mmol) and the corresponding diphosphine (0.100 mmol) was dissolved in CH_2Cl_2/MeOH (3/1, 10 mL) and the solution stirred at room temperature for 14 h. The yellow solutions were evaporated to dryness to give yellow solids. The solids were dissolved in the minimum volume of dichloromethane and then diethyl ether was poured. The yellow lemon solids obtained were filtered, washed with diethyl ether (3 x 10 mL) and dried under vacuum.

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})]$_2$(μ-dppm) (1$_2$-dppm): Yield 0.110 g (84%). Found: C, 49.81; H, 4.23; N, 2.20. Calc. for $C_{55}H_{54}Ir_2N_2O_8P_2$: C, 50.14; H, 4.13; N, 2.13. ^1H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 7.95-7.82 (m, 2H), 7.71 (d, 1H), 7.66-7.62 (m, 3H) (pydc), 7.21-7.10 (br m, 6H, Ph), 6.98-6.89 (br m, 6H, Ph), 6.80 (m, 4H, Ph), 6.64 (bd, 4H, Ph) (dppm), 5.46 (m, 1H), 5.24 (m, 1H), 5.17 (m, 2H) (=CH, C_8H_{13}), 2.83 (m, 2H), 2.36 (m, 2H), 2.27-1.98 (set of m, 6H), 1.77 (m, 2H), 1.59 (set of m, 4H), 1.34 (m, 2H), 1.19 (m, 2H), 0.80 (m, 2H), 0.57 (m, 2H) (>CH_2, C_8H_{13} and dppm). $^{31}P\{1H\}$ NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -10.96 (s), -11.64 (s). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 961.2 [$Ir(dppm)_2^+$]. MS (ESI, CH_3CN) *m/z*: 850.2 (M^+ - **1**).

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})]$_2$(μ-dppe) ($\mathbf{1}_2$-dppe). Yield 0.113 g (85%). Found: C, 50.39; H, 3.98; N, 2.01. Calc. for $C_{56}H_{56}Ir_2N_2O_8P_2$: C, 50.52; H, 4.24; N, 2.10. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 7.81 (t, 1H, J_{H-H} = 7.8 Hz), 7.79 (t, 1H, J_{H-H} = 7.8 Hz), 7.69 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz), 7.60 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz), 7.57 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz), 7.50 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz) (pydc), 7.40-7.10 (set of m, 12H), 6.97 (t, 2H, J_{H-H} = 8.4 Hz), 6.87 (m, 4H), 6.79 (t, 2H, J_{H-H} = 8.1 Hz) (Ph, dppe), 5.76 (t, 1H, J_{H-H} = 8.8 and 2.8 Hz), 5.66 (br m, 3H) (=CH, C_8H_{13}), 2.99 (d, 2H, J = 16.2 Hz), 2.43 (m, 2H), 2.13 (m, 4H), 2.0 (m, 2H), 1.90-1.65 (set of m, 6H), 1.59 (m, 2H), 1.35-1.15 (m, 4H), 0.80 (m, 2H), 0.63 (m, 2H) (>CH_2, C_8H_{13} and dppe). ^{13}C{^{1}H} NMR (100.63 MHz, 298 K, CD_2Cl_2): δ 171.18, 172.14, 171.63, 171.56 (*C*O), 145.72, 144.58 (C-2 and C-6), 138.16, 138.07 (C-4) (pydc), 133.0-132.23, 131.05, 130.91, 130.79, 130.60, 129.69-129.47 (Ph, dppe), 129.47, 129.40, 129.19, 129.12 (C-3 and C-5, pydc), 127.50-126.66 (C_{ipso}, Ph, dppe), 90.13, 89.45, 82.06, 81.45 (C-4 and C-5, C_8H_{13}), 37.47, 37.26 (>*C*H_2), 32.55 (dd, J_{C-P} = 90.0 and 2.2 Hz, C-1), 32.56, 32.39 (>*C*H_2), 32.41 (dd, J_{C-P} = 90.0 and 2.2 Hz, C-1) (C_8H_{13}), 27.89 (t, J_{C-P} = 3.6 Hz, >*C*H_2), 27.73 (t, J_{C-P} = 3.6 Hz, >*C*H_2) (dppe), 26.43, 26.33, 23.51, 23.49, 17.04 (d, J_{C-P} = 7.3 Hz), 16.79 (d, J_{C-P} = 6.6 Hz) (>*C*H_2, C_8H_{13}). ^{31}P{^{1}H} NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -13.68 (s), -13.82 (s). MS (MALDI-Tof, DCTB, CH_2Cl_2) *m/z*: 989.2 [Ir(dppe)$_2^+$], 699.1 [Ir(C_8H_{13})(dppe)$^+$]. MS (ESI, CH_3CN) *m/z*: 1329.2 [M]$^+$, 864.2 (M$^+$ - **1**).

[Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})]$_2$(μ-dppp) ($\mathbf{1}_2$-dppp). Yield 0.112 g (83%). Found: C, 50.45; H, 4.31; N, 2.21. Calc. for $C_{57}H_{58}Ir_2N_2O_8P_2$: C, 50.88; H, 4.34; N, 2.08. ^{1}H NMR (400.16 MHz, 298 K, CD_2Cl_2): δ 7.73 (t, 1H, J_{H-H} = 7.6 Hz,), 7.72 (t, 1H, J_{H-H} = 7.6 Hz) (4-H, pydc), 7.64 (dd, 1H, J_{H-H} = 7.8 and 1.3 Hz), 7.59 (dd, 1H, J_{H-H} = 7.6 and 1.3 Hz), 7.46 (br d, 1H, J_{H-H} = 7.6 Hz), 7.41 (br d, 1H, J_{H-H} = 7.3 Hz) (H-3 and H-5, pydc), 7.28 (t, 2H, J_{H-H} = 7.3 Hz,), 7.19-7.13 (set of m, 6H), 7.11-7.01 (set of m, 8H), 6.91 (t, 2H, J_{H-H} = 8.32 Hz), 6.79 (t, 2H, J_{H-H} = 8.4 Hz) (Ph, dppp), 5.77 (m, 2H), 5.66 (br t, 1H, J_{H-H} = 8.4 Hz), 5.58 (t, 1H, J_{H-H} =

8.4 Hz) (H-4 and H-5, pydc), 2.88 (d, 1H, J_{H-H} = 16.7 Hz), 2.79 (d, 1H, J_{H-H} = 16.2 Hz), 2.42-2.37 (m, 3H), 2.28-2.10 (m, 6H), 2.05-1.90 (m, 4H), 1.88-1.70 (m, 3H), 1.51 (t, 2H, J_{H-H} = 12.1 Hz), 1.27 (m, 4 H), 0.91-0.82 (m, 2H), 0.67-0.57 (m, 2H) (>CH_2, dppp and C_8H_{13}). $^{31}P\{^1H\}$ NMR (161.99 MHz, 298 K, CD_2Cl_2): δ -17.12 (s), -18.10 (s). MS (ESI, CH_3CN) *m/z*: 879.2 (M^+ - **1**).

Theoretical Calculations. All computations were performed using the Gaussian 09 (RevB.01) package.[45] The structures fully optimized without geometrical constraints and the stationary points (minima and TS) were confirmed by frequency calculations. The connection between the transition states and the minima were checked by visual inspection of the negative frequency calculation and an extensive IRC calculation in both directions was performed for the transition state $TS_{4\text{-}4b}$. The calculations were carried out using the B3LYP functional and the basis sets used were: LANL2DZ supplemented with an f function and its associated ECP for iridium,[46] and 6-31G** for the rest of atoms. The structures of the optimized molecules were depicted with the CyLview program.[47]

Crystal structure determination. Data collection was performed at low temperature (100(2)K) on a Bruker SMART APEX CCD (**1-py** and **1-dppm**) or on a Bruker APEX DUO (**7**) diffractometers equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using narrow frames (0.3˚ in ω). Cell parameters were refined from the observed setting angles and detector positions of strong reflections (31 744 refl., $2\theta \leq 30.27°$ (**7**); 9 435 refl., $2\theta \leq 28.85°$ (**1-py**); 894 refl., $2\theta \leq 16.57°$ (**1-dppm**)). Data were corrected for Lorentz and polarization effects using SAINT-PLUS,[48] and a multiscan absorption correction was applied with SADABS program.[49] The structure was solved by Patterson or direct methods and completed by successive difference Fourier syntheses (SHELXS-86).[50] Refinement was carried out by full-matrix least-squares on F^2 with SHELXL97,[51] including isotropic and

subsequent anisotropic displacement parameters for all non-hydrogen atoms. Treatment of hydrogen atoms and detected static disorder problems are described below.

Crystal data for **1-py**: $C_{20}H_{21}IrN_2O_4$, M_r = 545.59, monoclinic, space group $P2_1/n$, crystal size 0.221 × 0.203 × 0.023 mm, a = 9.6334(6), b = 15.3382(9), c = 13.2311(8) Å, β = 111.1380(10)°, V = 1 823.47(19) Å^3, Z = 4, ϱ_{calc} = 1.987 g cm^{-3}, μ(Mo$_{K\alpha}$) = 7.351 mm^{-1}. Min. and max. trans. fact. 0.293 and 0.849, 22 260 measured reflections (2.12 ≤ θ ≤ 28.86°), 4 476 unique (R_{int} = 0.0409); number of data/restraints/parameters 4 476/0/327; final R_1 = 0.0276 ($I > 2\sigma(I)$), wR_2 = 0.06373, S = 1.066 for all data; max difference peak/hole 1.972/–1.383 e Å^{-3}. Hydrogen atoms of the carboxylate and pyridine ligands were included in observed positions and refined as free isotropic atoms. Anomalous displacement parameters revealed the presence of static disorder involving 5 carbon atoms of the σ,π-cyclooctenyl ligand. Two fragments with complementary occupancies were included in the refinement. Carbon atoms with the lower occupancy were maintained isotropic, whereas those of higher occupancy were refined anisotropically. Hydrogen atoms were included in calculated positions for this disordered ligand.

Crystal data for **1-dppm**: $C_{40}H_{38}IrNO_4P_2$, M_r = 850.85, triclinic, space group P-1, crystal size 0.081 × 0.049 × 0.018 mm, a = 9.6225(13), b = 13.0524(17), c = 15.245(2) Å, α = 111.006(3), β = 95.558(3), γ = 103.966(3)°, V = 1 698.8(4) Å^3, Z = 2, ϱ_{calc} = 1.663 g cm^{-3}, μ(Mo$_{K\alpha}$) = 4.068 mm^{-1}. Min. and max. trans. fact. 0.734 and 0.930, 18 343 measured reflections (1.75 ≤ θ ≤ 25.68°), 6 428 unique (R_{int} = 0.1020); number of data/restraints/parameters 6 428/0/450; final R_1 = 0.0618 ($I > 2\sigma(I)$), wR_2 = 0.1071, S = 1.032 for all data; max difference peak/hole 1.107/–2.072 e Å^{-3}. Hydrogens were introduced in calculated positions and refined with positional and displacement riding parameters. An analogous static disorder of the σ,π-cyclooctenyl ligand to that described for 1-py was observed. A similar model based on two partial fragments was established for this molecule.

Crystal data for **7**: $C_{84}H_{130}Ir_4N_2O_8 \cdot 2\ CH_3OH$, $M_r = 2128.78$, tetragonal, space group $P4_2/n$, crystal size 0.329 × 0.127 × 0.096 mm, $a = 16.7340(7)$, $b = 19.659(2)$, $c = 28.8823(12)$ Å, $\beta = 106.824(2)°$, $V = 8087.8(6)$ Å^3, $Z = 4$, $\varrho_{calc} = 1.748$ g cm^{-3}, μ(MoKα) = 6.619 mm^{-1}. Min. and max. trans. fact. 0.242 and 0.428, 94357 measured reflections ($1.72 \le \theta \le 30.53°$), 11 887 unique ($R_{int} = 0.0323$); number of data/restraints/parameters 11 887/0/716; final $R_1 = 0.0256$ ($I > 2\sigma(I)$), w$R_2 = 0.0713$, $S = 1.069$ for all data; max difference peak/hole 1.870/–0.521 e Å^{-3}. Most of the hydrogen atoms of the metal cluster have been observed in the difference Fourier maps and refined as free isotropic atoms. A methanol solvent molecule was highly disordered among the metal complexes; two independent CO moieties (without hydrogen atoms) with complimentary occupancy factors were included in the model to account for the presence of this solvent.

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Supporting Information. X-ray crystallographic files in CIF format for the structure determination of compounds **1-py, 1-dppm** and **7**. Optimized coordinates for compounds **1** and **4**, intermediates **4a**-**4d**, and related transition states. Animation of the solvent-assisted proton transfer process in mov format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Choi, J.. MacArthur, A. H. R.. Brookhart, M.. Goldman, A. S. *Chem. Rev.* **2011**, *111*, 1761–1779. (b) Selander, N.. Szabó, K. J. *Chem. Rev.* **2011**, *111*, 2048–2076. (c) Leisa, W.. Mayera, H. A.. Kaska, W. C. *Coord. Chem. Rev.* **2008**, *252*, 1787–1797. (d) Albrecht, M. van Koten, G. *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781.

(2) *The Chemistry of Pincer Compounds*; Morales-Morales, D., Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007.

(3) (a) Romain, C.; Brelot, L.; Bellemin-Laponnaz, S.; Dagorne, S. *Organometallics* **2010**, *29*, 1191–1198. (b) Klein, A.; Elmas, S.; Butsch, K. *Eur. J. Inorg. Chem.* **2009**, 2271–2281. (b) Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2008**, *27*, 6123–6142. (c) Agapie, T.; Henling, L. H.; DiPasquale, A. G.; Rheingold, A. L.; Bercaw, J. E. *Organometallics* **2008**, *27*, 6245–6256.

(4) (a) O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 11185–11195. (b) Sarkar, S.; McGowan, K. P.; Kuppuswamy, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 4509–4512. (c) O'Reilly, M. E.; Del Castillo, T. J.; Abboud, K. A.; Veige, A. S. *Dalton Trans.* **2012**, *41*, 2237–2246. (d) Kuppuswamy, S.; Peloquin, A. J.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Organometallics* **2010**, *29*, 4227–4233.

(5) (a) Szigethy, G.; Heyduk, A. F. *Dalton Trans.* **2012**, *41*, 8144–8152. (b) Lu, F.; Zarkesh, R. A.; Heyduk, A. F. *Eur. J. Inorg. Chem.* **2012**, 467–470. (c) Heyduk, A. F.; Zarkesh, R. A.; Nguyen, A. I. *Inorg. Chem.* **2011**, *50*, 9849–9863. (d) Zarkesh, R. A.; Heyduk, A. F. *Organometallics* **2011**, *30*, 4890–4898.

(6) (a) Hartwig, J. F. *Acc. Chem. Res.* **2012**, *45*, 864–873. (b) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890–931. (c) *Activation and Functionalization of C-H Bonds*; Goldberg, K. I., Goldman, A. S. Eds.; ACS Symposium Series 885, American Chemical Society: Washington, DC, 2004. (d) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995***, 28*, 154–162.

(7) (a) Hashiguchi, B. G.; Bischof, S. M.; Konnick, M. M.; Periana, R. A. *Acc. Chem. Res.* **2012**, *45*, 886–898. (b) Bhalla, G.; Periana, R. A. *Angew. Chem. Int. Ed.* **2005**, *44*, 1540–1543, (c) Wong-Foy, A. G.; Bhalla, G.; Lui, X. Y.; Periana, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 14292–14293. (d) Matsumoto, T.; Taube, D. J.; Periana, R. A.; Taube, H.; Yoshida, H. *J. Am. Chem. Soc.* **2000**, *122*, 7414–7415.

(8) Bhalla, G.; Lui, X. Y.; Oxgaard, J.; Goddard, W. A.; Periana, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 11372–11389.

(9) Weinberg, D. R.; Hazari, N.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2010**, *29*, 89–100.

(10) Fu, R.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **2011**, *30*, 6751–6765.

(11) Nguyen, D. H.; Pérez-Torrente, J. J.; Lomba, L.; Jiménez, M. V.; Lahoz, F. J.;. Oro, L. A *Dalton Trans.* **2011**, *40*, 8429–8435.

(12) (a) Sengupta, S. K.; Sahni, S. K.; Kapoor, R. N. *Polyhedron* 1983, **2**, 317–322. (b) Matthews, R. W.; Hamer, A. D.; Hoof, D. L.; Tisley, D. G.; Walton, R. A. *Dalton Trans.* 1973, **10**, 1035–1038.

(13) Some examples of iridium σ,π-cyclooctenyl complexes: (a) Pontiggia, A. J.; Chaplin, A. B.; Weller, A. S. *J. Organomet. Chem.* **2011**, *696*, 2870–2876. (b) Safronov, A. V.;

Zinevich, T. V.; Dolgushin, F. M.; Tok, O. L.; Vorontsov, E. V.; Chizhevsky, I. T. *Organometallics* **2004**, *23*, 4970–4979. (c) Martin, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406–5417. (d) Mønsted, L.; Mønsted, O.; Schäffer, S.; Simonsen, K.; Søtofte, I. *Acta Chem. Scand.* **1996**, *50*, 973–978. (e) Esteruelas, M. A.; Olivan, M.; Oro, L. A.; Schulz, M.; Sola, E.; Werner, H. *Organometallics* **1992**, *11*, 3659–36664.

(14) (a) Yamagata, T.; Tadaoka, H.; Nagata, M.; Hirao, T.; Kataoka, Y.; Ratovelomanana-Vidal, V.; Genet, J. P.; Mashima, K. *Organometallics* **2006**, *25*, 2505–2513. (b) Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, ***32***, 1681–1688. (c) van Doorn, J. A.; Masters, C.; van der Woude, C. *J. Chem. Soc. Dalton Trans.* **1978**, 1213–1220.

(15) Elliott, P. I. P.; Haslam, C. E.; Spey, S. E.; Haynes, A. *Inorg. Chem.* **2006**, *45*, 6269–6275.

(16) Åkermark, B.; Martin, J.; Nyström, J. -E.; Strömberg, S.; Svensson, M.; Zetterberg, K.; Zuber, M. *Organometallics* **1998**, *17*, 5367–5373.

(17) (a) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M.; *Organometallics* **1999**, *18*, 3061–3069. (b) Hoel, G. R.; Stockland, R. A. Jr.; Anderson, G. K.; Ladipo, F. T.; Braddock-Wilking, J.; Rath, N. P.; Mareque-Rivas, J. C. *Organometallics* **1998**, *17*, 1155–1165.

(18) Su, Y.; Song, G.; Han, K.; Li, X. *J. Organomet. Chem.* **2011**, *696*, 1640–1646.

(19) Wang, W. -H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. *ACS Catal.* **2013**, *3*, 856–860.

(20) Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Ortuño, M. A.; Ujaque, G.; Lledos, A. *Inorg. Chem.* **2013,** DOI: 10.1021/ic401119p.

(21) Kovacs, G.; Lledos, A.; Ujaque, G. *Organometallics* **2010**, *29*, 3252–3260.

(22) Campos, J.; Espada, M. F.; López-Serrano, J.; Carmona, E. *Inorg. Chem.* **2013**, *52*, 6694–6704.

(23) (a) Zangl, A.; Klufers, P.; Schaniel, D.; Woike, T. *Dalton Trans* **2009**, 1034–1045. (b) Takuma, M.; Ohki, Y.; Tatsumi, K. *Organometallics* **2005**, *24*, 1344–1347. (c) Suh, I. -H.; Lee, J. -H.; Song, J. -H.; Oh, M. -R.; Suh, J. -S.; Park, S. -J.; Lee, K. -W. *J. Korean Phys. Soc.* **1996**, *29*, 739–744.

(24) (a) Dominguez-Martin, A.; Choquesillo-Lazarte, D.; Gonzalez-Perez, J. M.; Castineiras, A.; Niclos-Gutierrez, J. *J. Inorg. Biochem.* **2011**, *105,*1073–1080. (b) Meier, R.; Molinier, M.; Anson, C.; Powell, A. K.; Kallies, B.; van Eldik, R. *Dalton Trans.* **2006**, 5506–5514.

(25) Khokhar, R.; Xu, Q.; Al-Baker, S.; Bear, J. L. *Inorg. Chim. Acta* **1992**, *194*, 243–246.

(26) (a) Alonso, P. J.; Benedí, O.; Fabra, M. J.; Lahoz, F. J.; Oro, L. A.; Pérez-Torrente, J. J. *Inorg. Chem.* **2009**, *48*, 7984–7993. (b) Rodman, G. S.; Mann, K. R. *Inorg. Chem.* **1988**, *27*, 3338–3346.

(27) Bombi, G. G.; Aikebaier, R.; Dean, A.; Di Marco, V. B.; Marton, D.; Tapparo, A. *Polyhedron* **2009**, *28*, 327–335.

(28) Mirti, P.; Gennaro, M. C. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1259–1264.

(29) Schwarzenbach, G.; Anderegg, G.; Schneider, W.; Senn, H. *Helv. Chim. Acta* **1955**, *38*, 1147–1171.

(30) Alley, W. M.; Girard, C. W.; Ozkar, S.; Finke, R. G. *Inorg. Chem.* **2009**, *48*, 1114–1121.

(31) Feldman, J.; Calabrese, J. C. *Inorg. Chem.* **1994**, *33*, 5955–5956.

(32) (a) Böttcher, H. C.; Graf, M.; Mayer, P.; Sunkel, K.; Kruger, H. *Inorg. Chim. Acta* **2011**, *365*, 103–107. (b) Geier, M. J.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Eur. J. Inorg. Chem.* **2010**, 4602–4610. (c) Cheung, W. -M.; Lai, C. -Y.; Zhang, Q. -F.; Wong, W. -Y.; Williams, I. D.; Leung, W. -H. *Inorg. Chim. Acta* **2006**, *359*, 2712–2720.

(33) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans.* **1987**, S1–S19.

(34) Bhalla, G.; Oxgaard, J.; Goddard III, W. A.; Periana, R. A. *Organometallics* **2005**, *24*, 5499–5502.

(35) Atkinson, K. D.; Cowley, M. J.; Elliot, P. I. P.; Duckett, S. B.; Green, G. G. R.; López-Serrano, J.; Whitwood, A. C. *J. Am. Chem. Soc.* **2009**, *131*, 13362–13368.

(36) Kanematsu, N.; Ebihara, M.; Kawamura, T. *J. Chem. Soc. Dalton Trans.* **1999**, 4413–4417.

(37) Data obtained from an specific search on CSD: Allen, F. H. *Acta Cryst.* **2002**, B58, 380–388.

(38) (a) Nabavizadeh, S. M.; Haghighi, M. G.; Esmaeilbeig, A. R.; Raoof, F.; Mandegani, Z.; Jamali, S.; Rashidi, M.; Puddephatt, R. J. *Organometallics* **2010**, *29*, 4893–4899. (b)

Martínez, J.; Adrio, L. A.; Antelo, J. M.; Ortigueira, J. M.; Pereira, M. T.; Fernández, J. J.; Fernández, A.; Vila, J. M. *J. Organomet. Chem.* **2006**, *691*, 2721–2733. (c) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *Inorg. Chim. Acta* **2003**, *347*, 41–48.

(39) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707–2717.

(40) Chaplin, B.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inor. Chem.* **2005**, 4762–4774.

(41) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126–130.

(42) Ortmann, D. A.; Werner, H. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1373–1376.

(43) Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. A* **1971**, 2334–2337.

(44) Nishiyama, H.; Yamaguchi, M.; Kondo, M.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 4306–4309.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.01 2009.

(46) Ehlers, A.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111–114.

(47) Legault, C. Y. CyLview, Université de Sherbrooke, 2009, Canada.

(48) SAINT-PLUS, version 6.01, 2001, Bruker AXS, Inc; Madison, USA.

(49) SADABS, Area-Detector Absorption Correction Program, 2001, Bruker-AXS, Inc; Madison, USA.

(50) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473. (b) Sheldrick, G. M. *Methods Enzymol.* **1997**, *276*, 628–641.

(51) (a) G. M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997. (b) G.M. Sheldrick, *Acta Crystallogr. Sect. A: Fundam. Crystallogr.* **2008**, *64*, 112–122.